# The Journal of the American Leather Chemists Association

American Leather Chemists Association

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# American Leather Chemists Association

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## The American Leather Chemists Association

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## COLOR TESTS WITH SKIVERS.

*By Oscar Riethof.*

Since the founding of the A. L. C. A., the desire to find a reliable method of determining the color that a vegetable tanning agent will produce on hide has been the cause of a great deal of work, both committee and individual, without bringing about the adoption of an official method for color testing. This is regrettable, as the lack of an official method for color tests creates daily differences between the parties involved. At present, nearly every chemist has his own way in this matter, and is obtaining results which up to a certain limit have a comparative value for his own work of control, yet the moment his own work has to stand a comparison with that of other laboratories, the lack and disadvantage of not having an official method becomes apparent, and makes the individual's work quite valueless.

There seems to be very little difference of opinion among the members of the A. L. C. A. as to the advisability and even necessity of using hide for color test purposes. The question of employing animalized cotton, broadcloth, hide powder, etc., seems fairly well settled, and the colorimeter, however great its value may be, belongs to a class of colorimetric work that we will leave out of discussion. In the following article I will, therefore, confine myself exclusively to color tests obtained, and obtainable, by using hide.

I will first attempt to specify the reasons why the results obtained on hide differ so greatly. They are, namely, (1) the kind

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of hide or skin used for the skivers, (2) its preparation and preservation, (3) the part of the hide or skin used for the skivers, (4) the strength of the solution, (5) the quantity of tanning and coloring matter used, compared with the weight of the hide taken, (6) the thickness of the skiver, (7) the time the skiver is left in the solution, (8) the question of agitating, versus laying-away, and (9) the question of finishing, including the intensity of washing, the oiling and the conditions of drying. These are the most important points that influence the final results, and only after settling all of them, and others not mentioned, may we hope to develop a method that will give satisfaction.

First turning our attention to the question of which is the most suitable hide material to use, we may have the choice of calfskin, cow-split, whole sheepskins, or sheep skivers. In making color tests we must always keep in mind that the aim is not to get from a certain extract a skiver as light as possible, but to show to the tanner what color he may expect on his stock from the product in question. That the same extract gives a different shade on sheepskin and on cow-splits, is well known, and has been up for discussion at former meetings of the A. L. C. A. In this I agree with Armstrong[1] who believes sheepskins quite unsatisfactory, since the color obtained is too light, and does not represent the color shown on the tanned leather. From many sides it has been pointed out how unsatisfactory sheepskins are, as even if one happens to strike a good skin, only the best parts are available for comparative tests.[2] In this respect the use of grain cow-splits has a distinct advantage, as then only the bend is used for color tests, while the rest of the hide including the flesh-split, may be used for other purposes. In the end, therefore, splits are not at all expensive. It follows that if only for the reason that certainly over 90 per cent. of color tests are made for tanners of heavy hides, I consider that the question of using sheepskins in any form, is settled.

To discuss calfskin does not seem necessary as the results obtained with it have not been very satisfactory. It is difficult to obtain good skins, their structure varies greatly, and there is the disadvantage of discarding a great deal of waste.

[1] JOURNAL 1913, p. 519.

[2] Veitch and Hurt, JOURNAL 1906, p. 114.

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The preparation and preservation of the hide material in boro-phenol, as practiced now and as described by Small a number of times, seems very satisfactory. It is important, however, to wash the skivers well before using, as boro-phenol seems to have a decided effect upon the color.[3] Another important observation is that sheepskins when taken from the boro-phenol and washed with cold water sometimes plump very much. Upon tanning, such plump skivers give a considerably darker shade. It seems that the boric acid has a great deal to do with this plumping. The writer, therefore, used lukewarm water for washing. The temperature of the water used in washing cow-splits seems to have no influence.

When we turn our attention to the tannin solution used, we find that the strength of the solution used by different chemists varies from ¼ to 4 per cent. Procter[4] suggests a ¼ per cent. solution, increasing to ½ per cent., as sufficient for thin grains, but says that the liquor can be raised to a much greater strength, with little darkening of color. It seems to the writer that the darkening effect of stronger solutions differs with the tanning material used.

The thing that is most important is not the strength of the liquor, but the proportion of coloring matter to the weight of the hide employed. This important fact is generally neglected. A step in the right direction was made by the 1913 Committee on Color Tests, when the use of 200 cc. of liquor was suggested, without, however, taking into consideration the fact that different workers may employ green skivers that vary greatly in weight.

Reed[5] brought attention to the fact that in the present form of color testing we are ignoring the first principle of true dye testing. The dye tester never employs more dye in the bath than the fabric is capable of exhausting. He says further, that the hide has undoubtedly the power of selective absorption. If we present, therefore, more color to the pelt than it has the power of affixing, it may take up certain colors to the exclusion of others. This is certainly true. But we must not forget that we cannot get a good skiver unless it is quite well tanned. We cannot expect,

[3] Kerr, JOURNAL 1911, p. 94.
[4] Leather Chemist's Pocket Book, p. 115.
[5] JOURNAL A. L. C. A., April, 1914.

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therefore, to decolorize and detannize the liquor completely, as the absorptive power of the partly tanned skin for the weakened liquor is so small as to make the desired result a matter of impossibility. What we can do is to allow only a slight excess of tannin. If we do this, we shall find that the liquor is practically decolorized.

Kerr[6] has done work along the same line. He suggests the exclusive use of cow-splits and does the coloring with a solution, the tannin content of which is 80 per cent. of the dry weight of the grain split. He recommends that the dry hide employed be not less than 2 grams nor more than 2.5 grams. The solution is measured into a shaker bottle, the grain entered, and shaking proceeded with until the solution is practically detannized. This will require six or seven hours; somewhat longer in the case of bark extracts.

The process seemed an encouraging one and was therefore tried out by the writer. The liquors left were in many cases nearly colorless; in other cases they were more or less colored, depending on the material tested, and the conditions mentioned below.

ANALYSIS OF LIQUORS USED IN THE EXPERIMENTS. Grams in 100 cc.

| | Hemlock | Oak bark | Chestnut | Quebracho |
|---|---|---|---|---|
| Total solids | 0.701 | 0.773 | 0.602 | 0.569 |
| Soluble solids | 0.669 | 0.749 | 0.591 | 0.553 |
| Insol. solids | 0.032 | 0.824 | 0.011 | 0.016 |
| Non-tannins | 0.269 | 0.349 | 0.191 | 0.153 |
| Tannins | 0.400 | 0.400 | 0.400 | 0.400 |
| Purity* | 59.80 | 53.40 | 67.68 | 72.33 |

* Figured on soluble solids.

These experiments suggested the desirability of finding out how much of the tannin is absorbed by the hide, in order to see if the suggested ratio of tannin to dry-hide weight—80 per cent. tannin on dry hide weight—was the best to use. At the same time tests were run using different percentages of tannin, and shaking different periods of time, in order to determine the conditions under which the most reliable results could be obtained. It seemed advisable to use for the experiments, in place of the 200 cc. of liquor with a tannin content of 80 per cent. of the dry

[6] JOURNAL A. L. C. A., 1914, p. 451.

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weight of the skiver, a liquor of analytic strength. This was done in order that all liquors should have the same strength, regardless of the size and weight of the skiver; and what is also of importance, it is possible to use for the color tests the remainder of the solution made up for analysis. In all cases more than 300 cc. of the 1,000 cc. made up, are at our disposal, and this amount is more than sufficient to tan a good sized skiver. The time required to make up a new solution is thus saved.

Of the two tables that follow, Table I shows the results of a series of tests carried on to show what influence the time of shaking had on the results. In all cases a liquor of analytic strength was prepared and a sufficient volume of this used to contain 80 per cent. of the dry skiver weight, in tannin. A study of the table clearly shows that the most suitable time for drumming is six hours, as the percentage of tannin absorbed after this time is so low that no advantage results from longer drumming. No difference can be noticed between the shade of the skivers run six hours and the shade of those run twenty-four hours. It is with regret that the writer is not able to bring before the reader the skivers obtained in these tests, as they would greatly aid in explaining the results shown in the tables.

The theoretical degree of tannage $\frac{\text{Comb. tannin} \times 100}{\text{hide substance}}$ is in all cases about 50 per cent., and indicates that the skivers were tanned without having absorbed more tannin than necessary. It seemed to the writer that it might be possible to use less than 80 per cent. tannin on dry-hide weight, as even after twenty-four hours drumming only about two-thirds of the tannin was absorbed. To determine this a series of experiments was carried on using from 50 per cent. to 80 per cent. of tannin on dry-hide weight. For these tests the time of shaking was six hours. The results are shown in Table II.

By using less tannin it was possible to detannize more completely, as the percentage of tannin absorbed went as high as 83 per cent. It was found, however, that, working with considerably less than 80 per cent. of tannin the skiver was not tanned very well, especially when thick skivers were used. The table shows that the degree of tannage is only about 40 per cent. The writer,

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TABLE I.—PERCENTAGE OF TANNINS ABSORBED BY COW-SPLIT SKIVERS DURING DIFFERENT TIMES OF DRUMMING. ANALYTICAL STRENGTH.

| Time of drumming (Hrs.) | Skiver | | | Cc. liquor used | Spent liquor | | | Percentage of tannins absorbed | Degree of tannage |
|---|---|---|---|---|---|---|---|---|---|
| | Wet weight (Gms.) | Thickness tanned, dry (mm.) | Area (sq. cm.) | | Tannins (Per cent.) | Non-tannins (Per cent.) | Purity (Per cent.) | | |
| *Hemlock Extract* | | | | | | | | | |
| 4 | 5.2 | 0.3 | 56 | 156 | 0.156 | 0.299 | 34.28 | 61.00 | 48.85 |
| 6 | 6.0 | 0.4 | 56 | 180 | 0.155 | 0.297 | 34.29 | 61.25 | 49.00 |
| 24 | 6.0 | 0.5 | 60 | 204 | 0.133 | 0.287 | 28.25 | 66.75 | 53.40 |
| *Oak Bark Extract* | | | | | | | | | |
| 4 | 6.7 | 0.3 | 63 | 201 | 0.186 | 0.321 | 36.69 | 53.50 | 42.80 |
| 6 | 6.8 | 0.4 | 60 | 204 | 0.179 | 0.433 | 34.89 | 55.25 | 44.22 |
| 24 | 6.7 | 0.4 | 60 | 201 | 0.139 | 0.316 | 30.55 | 65.25 | 52.20 |
| *Chestnut Extract* | | | | | | | | | |
| 4 | 9.8 | 0.5 | 51 | 294 | 0.188 | 0.215 | 46.65 | 53.00 | 42.38 |
| 6 | 5.3 | 0.3 | 56 | 159 | 0.140 | 0.210 | 40.00 | 65.00 | 51.95 |
| 8 | 8.3 | 0.5 | 62 | 249 | 0.134 | 0.215 | 38.00 | 66.50 | 53.17 |
| 24 | 5.6 | 0.35 | 64 | 168 | 0.122 | 0.217 | 35.99 | 69.50 | 55.59 |
| *Quebracho Extract* | | | | | | | | | |
| 4 | 5.0 | 0.2 | 63 | 150 | 0.169 | 0.114 | 59.72 | 57.75 | 46.26 |
| 6 | 7.0 | 0.45 | 60 | 210 | 0.143 | 0.117 | 55.00 | 64.25 | 51.43 |
| 8 | 8.1 | 0.6 | 49 | 243 | 0.124 | 0.115 | 51.90 | 69.00 | 55.22 |
| 24 | 9.8 | 0.6 | 72 | 294 | 0.124 | 0.117 | 51.45 | 69.00 | 55.18 |

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TABLE II.—COW-SPLIT SKIVERS TANNED WITH DIFFERENT PERCENTAGES OF TANNINS. TIME OF DRUMMING SIX HOURS, ANALYTICAL STRENGTH.

| Percentage of tannins to dry hide weight | Skiver | | | Cc. liquor used | Spent liquor | | | Percentage of tannins absorbed | Degree of tannage |
|---|---|---|---|---|---|---|---|---|---|
| | Wet weight (Grams) | Thickness tanned dry (mm.) | Area (Sq. cm.) | | Tannins (Per cent.) | Non-tannins (Per cent.) | Purity (Per cent.) | | |
| *Hemlock Extract.* | | | | | | | | | |
| 50 | 6.7 | 0.40 | 67 | 125 | 0.090 | 0.258 | 25.86 | 77.38 | 38.80 |
| 60 | 6.4 | 0.40 | 49 | 144 | 0.127 | 0.260 | 32.86 | 68.25 | 41.00 |
| 70 | 7.0 | 0.65 | 52 | 184 | 0.110 | 0.269 | 29.00 | 72.50 | 51.00 |
| 80 | 6.8 | 0.50 | 65 | 204 | 0.130 | 0.265 | 32.91 | 67.50 | 54.00 |
| *Oak Bark Extract.* | | | | | | | | | |
| 50 | 6.2 | 0.30 | 65 | 116 | 0.099 | 0.314 | 23.97 | 75.25 | 37.53 |
| 60 | 7.0 | 0.35 | 63 | 157 | 0.116 | 0.330 | 26.00 | 71.00 | 42.50 |
| 70 | 7.6 | 0.40 | 68 | 199 | 0.133 | 0.334 | 28.48 | 66.75 | 50.00 |
| 80 | 7.2 | 0.45 | 62 | 216 | 0.157 | 0.357 | 30.54 | 60.75 | 56.60 |
| *Chestnut Extract.* | | | | | | | | | |
| 50 | 7.3 | 0.50 | 49 | 137 | 0.077 | 0.190 | 28.84 | 80.75 | 40.46 |
| 60 | 6.4 | 0.50 | 49 | 144 | 0.092 | 0.183 | 33.46 | 77.00 | 46.25 |
| 70 | 7.7 | 0.55 | 64 | 202 | 0.100 | 0.187 | 34.84 | 75.00 | 52.47 |
| 80 | 6.3 | 0.45 | 64 | 189 | 0.106 | 0.201 | 34.52 | 73.50 | 58.84 |
| *Quebracho Extract.* | | | | | | | | | |
| 50 | 5.3 | 0.35 | 50 | 94 | 0.066 | 0.157 | 29.59 | 83.50 | 39.50 |
| 60 | 7.7 | 0.50 | 56 | 173 | 0.110 | 0.147 | 42.80 | 72.50 | 43.46 |
| 70 | 6.6 | 0.50 | 58 | 173 | 0.120 | 0.161 | 42.70 | 70.00 | 48.00 |
| 80 | 7.1 | 0.50 | 64 | 213 | 0.126 | 0.158 | 44.37 | 68.50 | 64.25 |

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therefore, concluded that the most suitable amount of tannin to use is 80 per cent., based on the dry weight of the skiver. Even a somewhat higher percentage would be all right, provided it was fixed for all workers.

The two tables also furnish interesting information as regards the speed at which different tanning materials are absorbed by the hide. As might be expected, the wood tannins—chestnut and quebracho—tan faster than the bark tannins. Another interesting feature is the little difference in the non-tannin figure. It can readily be seen that this percentage is nearly constant regardless of the time of drumming. In weaker liquor (Table II) the hide takes up some non-tannin.

At some places the tables show a little irregularity. This may be due in part to the use of wet hide in the experiments, which makes it difficult to work with great accurateness; it may be due in part to other analytical errors; but it was found that the greatest source of divergence, in the results as well as in the shade of the skivers, was due to the varying thickness of the splits. Why the area of the skiver employed is of great importance needs no explanation. A small thick skiver will certainly absorb the tannin and coloring matter slower than a thin one of the same weight. This makes it necessary to confine the thickness of the skiver material within certain limits. It was found that a finished skiver about ½ millimeter thick is the most suitable. If the material is too thick, the finished product may show a raw streak, with its known darkening effect upon the color. I would recommend that such heavy parts of the split be used for tests where the time of tanning is immaterial. The tanning may then be continued a greater length of time. We must always expect a certain irregularity in the thickness of the skiver material, as even with the best machines, the most skilled workmen and the utmost care, it is impossible to get a green split of uniform thickness.

It can be seen on the skivers obtained, whose thickness ran between 0.2 millimeter and 0.65 millimeter, that the influence on the shade is quite small. A heavy skiver will certainly show a deeper color than a thin one of greater area, since the same amount of coloring matter is absorbed by a smaller surface.

For the sake of completeness, it seemed advisable to carry on

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the same experiments with sheepskin. For this purpose a specially prepared lambskin was secured from the Hoppenstedt laboratory. This was cut into pieces of suitable size and washed the same as the grain split—three times with distilled water at room temperature. As said before, the skivers swelled up very much and were used in this condition for the experiments. The tests were carried on with different percentages of tannin, ranging from 60 per cent. to 150 per cent. and two splits were run at the same time for comparison.

The results are shown in Table III. We see here that the absorption by sheepskin is much slower than by grain splits. In no case is the exhaustion of the liquor so complete, or what is the same thing, is the degree of tannage so high, as with splits. The results are very irregular, in spite of the fact that the same care was taken as with splits. The same is true of the skivers obtained. The principal reasons for this were undoubtedly the plumping effect of the cold water, from whatever cause, and the fact that all parts of the skin were used.

I wish to call attention to the great amount of liquor of analytical strength that was needed for the tests with sheepskin. This made it impossible to employ the remainder of the solution used for analysis.

Besides whole sheepskins, hand skived and split skivers are in use. On account of their greater evenness, these would show more regularity in the results; but still—they are sheepskins, with all their faults. Results with these would be interesting, but lack of time has prevented the writer from trying these out.

Many laboratories are not equipped for shaking several hours; but the same degree of absorption and the same shade may be obtained by laying away in the liquor for a certain time, with occasional shaking.

Tests of this kind were carried on with splits and sheepskin. The time for shaking was reduced to half an hour, total time of tanning twenty-four hours, with occasional shaking by hand to insure evenness in color. The results are presented in Table IV and show that the percentage of absorption is about the same as with six hours drumming.

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TABLE III.—SHEEPSKIN AND COW GRAIN SPLIT SKIVERS TANNED WITH DIFFERENT PERCENTAGE OF TANNINS. SIX HOURS DRUMMING ANALYTICAL STRENGTH.

*Hemlock Extract*

| Percentage of tannins to dry hide-weight | Skiver | | | | Cc. liquor used | Spent liquor | | | Percentage of tannins absorbed | Degree of tannage |
|---|---|---|---|---|---|---|---|---|---|---|
| | Wet weight (grams) | Thickness tanned, dry (mm.) | Area (sq. cm.) | Kind | | Tannins (Per cent.) | Non-tannins (Per cent.) | Purity (Per cent.) | | |
| 60 | 10.7 | 0.60 | 38 | Sheepskin | 241 | 0.240 | 0.256 | 48.62 | 40.00 | 24.00 |
| 80 | 12.8 | 0.60 | 49 | " | 384 | 0.210 | 0.268 | 43.96 | 47.50 | 38.00 |
| 100 | 10.0 | 0.60 | 38 | " | 375 | 0.265 | 0.268 | 49 72 | 33.75 | 33.73 |
| 150 | 8.4 | 0.55 | 39 | " | 472 | 0.289 | 0.280 | 50.80 | 27.75 | 41.58 |
| 80 | 4.2 | 0.40 | 42 | Grain split | 126 | 0.115 | 0.231 | 33.23 | 71.25 | 57.00 |
| 150 | 4.0 | 0.40 | 42 | " " | 225 | 0.212 | 0.231 | 48.00 | 47.00 | 70.00 |
| | | | | *Oak Bark Extract* | | | | | | |
| 60 | 10.7 | 0.50 | 48 | Sheepskin | 241 | 0.241 | 0.277 | 46.52 | 39.75 | 25.53 |
| 80 | 10.2 | 0.50 | 35 | " | 306 | 0.293 | 0.283 | 50.88 | 26.75 | 21.50 |
| 100 | 8.2 | 0.55 | 48 | " | 307 | 0.256 | 0.297 | 46.30 | 36.00 | 35.90 |
| 150 | 10.0 | 0.55 | 47 | " | 563 | 0.321 | 0.296 | 52.03 | 19.75 | 30.00 |
| 80 | 4.8 | 0.30 | 55 | Grain split | 144 | 0.196 | 0.273 | 41.80 | 51.00 | 40.83 |
| 150 | 5.0 | 0.30 | 51 | " " | 281 | 0.286 | 0.289 | 49.73 | 28.50 | 42.80 |

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TABLE III. (*Continued.*)

*Chestnut Extract*

| Percentage of tannins to dry hide-weight | Skiver | | | | Cc. liquor used | Spent liquor | | | Percentage of tannins absorbed | Degree of tannage |
|---|---|---|---|---|---|---|---|---|---|---|
| | Wet weight (Grams) | Thickness (mm.) | Area (Sq. cm ) | Kind | | Tannins (Per cent.) | Non-tannin (Per cent.) | Purity Per cent.) | | |
| 60 | 12.3 | 0.70 | 40 | Sheepskin | 275 | 0.210 | 0.190 | 52.50 | 47.50 | 28.40 |
| 80 | 10.5 | 0.50 | 47 | " | 315 | 0.254 | 0.194 | 56.70 | 36.50 | 29.30 |
| 100 | 11.0 | 0.50 | 42 | " | 412 | 0.289 | 0.194 | 59.84 | 27.75 | 27.71 |
| 150 | 11.5 | 0.60 | 49 | " | 647 | 0.327 | 0.186 | 63.74 | 18.25 | 27.50 |
| 80 | 4.0 | 0.50 | 42 | Grain split | 120 | 0.131 | 0.171 | 43.10 | 67.25 | 53.83 |
| 150 | 3.2 | 0.35 | 35 | " " | 189 | 0.245 | 0.158 | 60.80 | 38.75 | 58.13 |
| | | | | *Quebracho Extract* | | | | | | |
| 60 | 5.8 | 0.60 | 35 | Sheepskin | 130 | 0.139 | 0.153 | 47.25 | 65.25 | 38.97 |
| 80 | 9.5 | 0.60 | 45 | " | 285 | 0.222 | 0.156 | 58.73 | 44.50 | 35.58 |
| 100 | 9.5 | 0.60 | 52 | " | 356 | 0.255 | 0.157 | 61.99 | 36.25 | 36.21 |
| 150 | 8.5 | 0.60 | 52 | " | 477 | 0.295 | 0.163 | 64.41 | 26.25 | 39.30 |
| 80 | 5.3 | 0.45 | 49 | Grain splii | 159 | 0.146 | 0.157 | 48.20 | 63.50 | 51.06 |
| 150 | 3.5 | 0.40 | 41 | " " | 197 | 0.238 | 0.156 | 60.40 | 40.50 | 60.76 |

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TABLE IV.—SKIVERS TANNED BY ½ HOUR DRUMMING AND LAYING AWAY WITH OCCASIONAL SHAKING FOR 24 HOURS.

*Oak Bark Extract.*

| Percentage of tannins to dry hide-weight | Skiver | | | | Cc. liquor used | Spent liquor | | | Percentage of tannins absorbed | Degree of tannage |
|---|---|---|---|---|---|---|---|---|---|---|
| | Wet weight (Grams) | Thickness (mm.) | Area (Sq. cm.) | Kind | | Tannins (Per cent.) | Non-tannins (Per cent.) | Purity (Per cent.) | | |
| 80 | 6.2 | 0.50 | 49.5 | Grain split | 186 | 0.164 | 0.288 | 36.28 | 59.00 | 47.20 |
| 80 | 7.5 | 0.55 | 49.5 | Sheep skin | 225 | 0.221 | 0.266 | 45.38 | 44.75 | 35.80 |
| 150 | 4.8 | 0.50 | 46.7 | Grain split | 270 | 0.271 | 0.277 | 49.45 | 32.25 | 48.38 |
| 150 | 11.4 | 0.60 | 56.0 | Sheep skin | 640 | 0.318 | 0.295 | 51.88 | 20.50 | 30.69 |
| | | | | *Chestnut Extract.* | | | | | | |
| 80 | 5.8 | 0.50 | 44.0 | Grain split | 174 | 0.139 | 0.177 | 44.00 | 65.25 | 52.20 |
| 80 | 9.5 | 0.60 | 52.0 | Sheep skin | 285 | 0.236 | 0.187 | 55.79 | 41.00 | 32.91 |
| 150 | 6.5 | 0.60 | 42.0 | Grain split | 365 | 0.261 | 0.186 | 58.39 | 34.75 | 52.03 |
| 150 | 7.5 | 0.60 | 49.0 | Sheep skin | 422 | 0.295 | 0.190 | 60.82 | 26.25 | 39.40 |

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It may be well at this juncture to describe the method used by the writer, in order that other members of the association may be able to try it out and form their own opinion as to its value. It would be interesting to bring other tanning materials into the course of the experiments, to see if they behave in a similar way to those used by the writer. The method is very similar to that given by Kerr.[7] It differs in the strength of the solution, as analytic strength (0.4 per cent.) is always used for reasons previously mentioned.

The dehydration with alcohol in place of tacking up and drying, as proposed by Kerr in the article mentioned, was tried, but it was found that grain as well as wood alcohol extracts a great deal of coloring matter, effecting the original shade decidedly. The writer's method is as follows:

Cut the grain split, as received from Small, into pieces of suitable size, and preserve in fresh boro-phenol solution (2 per cent. boric acid, 1 per cent phenol). Three by three inches is about the proper area for regular work.

In making skivers, wash three times in the shaker with distilled water for as many 15 minute periods. Shake off the free water and make a moisture determination in order to establish a factor for calculating the dry-hide content of other pieces. The writer finds that his own method of shaking off free water renders a skiver of approximately 15 per cent. dry hide, or hide-substance. This figure once established, weigh the grain piece to be used in a shallow dish, calculate its dry weight and the number of cubic centimeters of analytical strength liquor whose tannin content is equal to 80 per cent. of the dry-hide weight.

Measure this number of cubic centimeters into a shaker bottle, enter the skiver, and shake for six hours (alternative, shake one-half hour and let stand the rest of twenty-four hours). Squeeze out by hand, wash once with distilled water, shaking fifteen minutes, squeeze out again, tack on a board covered with clean blotting paper or filter paper, and dry slowly in a dark closet.

When liquors of analytic strength are used and the drying is done slowly, it is unnecessary to oil the grain and one cause for differences is thus eliminated. But if color tests, say for compar-

[7] JOURNAL A. L. C. A., 1914, page 454.

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ative work, are made with stronger solutions, oiling prevents darkening, and in this case the writer suggests the use of a limited and calculated amount of water-soluble oil, as fat liquor, applied in the shaker, thus avoiding an excess of oil with its known effect upon the shade.

The method outlined above makes it possible to get the finished skiver at the same time that the dishes come from the oven. This is of great importance to the trade chemist.

The writer would be very glad if other members of the association would try out this method, so that with it as a basis, we might possibly come nearer to the desired end of establishing an official method of color testing.

Wm. F. Mosser Company Chemical Laboratory,
Richwood, W. Va.

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## SOLE LEATHER VALUES.*

*By M. I. A. L. T. C.*

It was recently brought to the notice of the writer that certain American sole leathers are being offered to boot manufacturers at prices which, to say the least, prejudiced the sale of English sole leather, which of course, always fetches higher prices on the strength of its reputation for purity, and its better finish and color.

The usual phases of the old topic of the adulteration of American sole leather must be well known to readers of this JOURNAL, so that in this article it is not proposed to run over the same ground again in extenso. I have therefore analyzed four American leathers, together with three English leathers, and it will be all sufficient to discuss the interesting data obtained, which throw a vivid light upon a newer phase of the question.

It is now well known that there is not one pure oak bark tanner in the whole length and breadth of the British Isles. His epitaph was inscribed more than a decade ago, and his ever-to-be-regretted departure was brought about by modern methods, forced upon us by keen foreign competition. Those who would not keep the pace and modernize were ruined, or forced to close down, for

*Leather Trades' Review*, Nov. 10, 1915.

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successful competition demanded a quicker turnover and a heavier leather. That is where the chemist came in. He it was who in-

ANALYTICAL DATA (PER CENT.)

| | A. | B. | C. | D. | O. | X. | S. |
|---|---|---|---|---|---|---|---|
| Hide substance | 36.63 | 35.52 | 36.63 | 32.07 | 36.32 | 38.23 | 37.10 |
| Water soluble matters | 31.40 | 31.20 | 22.10 | 26.90 | 32.00 | 22.00 | 21.10 |
| Insoluble ash | 0.50 | 0.90 | 0.36 | 0.60 | 0.58 | 0.68 | 0.00 |
| Combined tanning matters | 19.37 | 18.66 | 28.65 | 28.21 | 17.00 | 26.31 | 25.20 |
| Moisture | 12.10 | 13.72 | 12.26 | 12.22 | 14.10 | 12.78 | 16.00 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Soluble ash | 0.72 | 1.80 | 0.20 | 1.80 | trace | trace | trace |
| Dry glucose | 1.85 | 9.76 | 3.42 | 5.44 | trace | trace | trace |
| Epsom salts | traces | 4.85 | traces | 4.53 | 1.6 | trace | — |
| | lb. oz. | lb. oz. | lb. oz. | lb. oz. | lb. oz. | lb. oz. | lb. oz. |
| Weight of 1 square foot | 1 6.1 | 1 9.1 | 1 4.8 | 1 4.6 | 1 10.3 | 1 7 | 1 8.5 |
| Area of 1 lb. leather in sq. in. | 104.1 | 91.6 | 110.9 | 111.7 | 87.6 | 100.5 | 94.2 |
| Price per square foot | 5s. | 3s. | 2s. | 2s. | 5s. | 3s. | 5s. |
| | 6½d. | 9½d. | 11d. | 7d. | 9d. | 5½d. | 2¾d. |

vented extracts (Paul Gondolo, a Frenchman, was the original inventor; Miller's were the first to take it up in this country, and Edwin Ellis was the first tanner to use it), and this spelt the first great advance towards quicker methods. Chemistry has played a great part in this movement. Only six years ago English sole leather was not expected to contain more than 20 per cent. of water soluble matters, but the present tendency is to still further speed up the tanning by mechanical methods, and the Federation limit for water solubles is now 25 per cent. In view of these facts, the following information and figures will prove very interesting:

SELLER'S DESCRIPTIONS OF LEATHERS EXAMINED.

A. Taken from a first-class English tannage of heavy bends. Tanner quotes (September) 3s. 8d., but would not sell without 14-pound and 16-pound bends, so that the real quotation would be about 4s. per pound.

B. Taken from Trust (American) scoured oak bends. The highest price made, 2s. 5d. These bends are just as good on the grain as sample A; better pattern; no brands.

C. Taken from Trust unscoured oak bends. Price 2s. 3d. Would wear even better than scoured.

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D. Taken from bends made by American packers. Price about 2s. These were put on the No. 2 pattern British Army boot, and are, of course, hemlock tanned. Pattern not so good as English.

O. English bends, sample slightly under full 5/16 inch, but was cut near belly edge to avoid loss of best part of butt, which is naturally slightly thicker and probably a little firmer. Price 3s. 6d per pound.

X. High-grade bark tanned leather, tanned in Kentucky or Virginia with oak bark. Warranted vat tanned, old-time process, probably 12 months in pits. Average 14 pound cut short to about 4 feet 4 inches. Cut straight both in shoulder, and belly, and can be sold at 2s. 4d. to 2s. 6d. according to selection, as against English tanned bends, made from various country hides, at from 3s. 4d. to 3s. 6d. per pound.

S. One of the best tannages in England. Straight vat tannage of long duration. Old-time process, little modernized. Price about 3s. 5d. per pound.

These figures prove the superiority of S leather to the others. The soluble matter is very low, showing that no attempt has been made to get excessive weight by loading with extracts.

The other two English leathers, A and O, were sent as being representative of English tannages (north of England), and the figures are disappointing. The soluble matter is higher than in the American tannages, and although the leathers are not adulterated in the sense that they contain sugars or mineral salts to any great extent (the Epsom salts in O is probably not intentionally added, and was most likely introduced by the use of hard water or tanning extracts containing magnesium salts), yet they show 6 to 7 per cent. of solubles above the Federation limit, and consequently are loaded to that extent with tanning extracts.

The combined tannin is low, proving rapid tannage by use of liquors of high concentration, and probably,too, by mechanical means, to get the extract in. That this form of loading is about as bad as that adopted by the Americans, using glucose and Epsom salts, is seemingly borne out by the water absorption test. Loading with extracts is regarded as more or less legitimate, and it is commonly thought that if tan extract does not help to resist moisture by filling the fibers, it, at least, does not attract it. The contrary

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would seem to be the case from a superficial study of the water absorption table.

Of the American leathers, B appears to be worst, although it makes nearly the best price. It is highly adulterated, undertanned, or very rapidly tanned, and cuts up the least economically, as shown by its small area. C and X would seem to be superior to A and O (English). The soluble matter is low, the combined tan is high, showing that the leather is well tanned; and C is only slightly adulterated. Although highly adulterated, D seems to be well tanned.

The pieces of leather submitted for analysis were not large enough for a water penetration test, so the absorption of water was estimated by cutting samples, 1 inch square, and placing them in 50 cc. of distilled water. They were weighed after soaking for various lengths of time, the increase in weight being due to water absorbed. At the termination of the test, the soluble matters soaked out were also estimated. The results of these tests are seen in the table below:

Weight of 1 square inch of leather in grams.

| A. | B. | C. | D. | O. | X. | S. |
|---|---|---|---|---|---|---|
| 4.358 | 4.952 | 4.088 | 4.061 | 5.176 | 4.514 | 4.811 |

Water absorbed by 1 square inch leather in grams.

| Hours | A. | B. | C. | D. | O. | X. | S. |
|---|---|---|---|---|---|---|---|
| ¼ | 1.080 | 0.673 | 1.037 | 0.537 | 1.137 | 0.732 | 0.831 |
| 1 | 1.106 | 0.790 | 1.070 | 0.631 | 1.165 | 0.834 | 1.071 |
| 3 | 1.113* | 0.864 | 1.083 | 0.705 | 1.197 | 0.941 | 1.160 |
| 6 | 1.105 | 0.896 | 1.099 | 0.739 | 1.255 | 1.016 | 1.197 |
| 24 | 1.082 | 0.936* | 1.117* | 0.745* | 1.392* | 1.089 | 1.207* |
| 48 | 1.054 | 0.918 | 1.117 | 0.716 | 1.364 | 1.091* | 1.205 |

* Indicates the approximate time of maximum absorption.

Percentage of water absorbed by 1 square inch leather, calculated from above table.

| Hours | A. | B. | C. | D. | O. | X. | S. |
|---|---|---|---|---|---|---|---|
| ¼ | 24.78 | 13.59 | 25.37 | 13.22 | 21.97 | 16.21 | 17.25 |
| 1 | 25.37 | 15.96 | 26.17 | 15.54 | 22.51 | 18.47 | 22.25 |
| 3 | 25.53 | 17.45 | 26.49 | 17.36 | 23.13 | 20.84 | 24.11 |
| 6 | 25.35 | 18.10 | 26.88 | 18.19 | 24.25 | 22.50 | 24.88 |
| 24 | 24.82 | 18.91 | 27.32 | 18.34 | 26.89 | 24.12 | 25.09 |
| 48 | 24.18 | 18.54 | 27.32 | 17.63 | 26.35 | 24.17 | 25.04 |

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Even this does not represent the total weight of water taken up by the leather, for in the soaking a certain amount of soluble matter is washed out and replaced by water. In order, therefore, to get the true weight of water taken up (neglecting differences in density), we must add to the above weights the weight of extract or solubles washed out.

**Weight of solubles soaked out of 1 square inch leather by 50 cc. water in 48 hours in grams.**

| A. | B. | C. | D. | O. | X. | S. |
|---|---|---|---|---|---|---|
| 0.4536 | 0.6408 | 0.3384 | 0.5252 | 0.6240 | 0.3552 | 0.348 |

**Calculated to percentage on leather weight.**

| | | | | | | |
|---|---|---|---|---|---|---|
| 10.41 | 12.95 | 8.28 | 12.93 | 12.06 | 7.87 | 7.23 |

From these figures may be calculated the total absorption of water in 48 hours:

**Total absorption water in grams.**

| A. | B. | C. | D. | O. | X. | S. |
|---|---|---|---|---|---|---|
| 1.508 | 1.559 | 1.445 | 1.241 | 1.988 | 1.446 | 1.553 |

**Total percentage absorption on leather weight.**

| | | | | | | |
|---|---|---|---|---|---|---|
| 34.59 | 31.49 | 35.59 | 30.55 | 38.41 | 32.03 | 32.28 |

Paradoxical, therefore, as it may seem, the leathers most adulterated with easily soluble hygroscopic substances, and giving up the most soluble matter on soaking, are those which resist water penetration most, weight for weight, *viz.*, B and D, and the latter is even better than the others from the standpoint of area. This demands some explanation, and a little discussion of the subject will not be out of place.

That Epsom salts, and more especially glucose, do attract moisture, by the fact that they are more hygroscopic and more soluble than tannins, is proved by the high percentage of solubles soaked out, and if the impermeability of leathers was a direct function of the water soluble, the leathers B and D would naturally show up worst, and, moreover, the percentage absorption and solubles of O would be almost identical with A, which is not the case. All these facts only go to prove the correctness of the assumption that glucose and Epsom salts are less water resistant than tannin extract, and tend to diminish the quality of the leather.

It must be evident that if all other factors were equal, those leathers giving up most solubles would absorb most water. This is far from being the case, and a close study of the figures leads

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one to the conclusion that the upsetting factor is the physical condition of the leather. It has long been known that water penetration tests are of very little practical value as an indication of the water resistance of a tannage, as any figures may be got, depending upon the rolling and finishing of the leather. The finishing of the American leathers tells to their advantage. The adulterants are so soluble that it has little effect on keeping them in, but once they are out the leather is in a better physical condition to resist water, probably through harder or wetter rolling. Where only tanning extracts are present, the finish seems to have more influence, as in the cases of A and O, which are equally loaded. A was probably rolled in a wetter condition. Even S, which is an excellent leather, was not rolled wet enough.

Both the English leathers A and O are unsatisfactory, O being the worst of all the samples submitted, but it can hardly be said that these samples are representative. The most satisfactory leather is perhaps X, which is also one of the cheapest and cuts economically.

There is certainly some ground for the statement that the quality of sole leather is on the down grade, and steps should be taken to improve it. First, the absurd demand for a pale colored leather should cease. Paleness indicates bleaching, and bleaching means partial destruction. The appearance of a leather is no indication of its quality.

Then the leather might be rolled as wet as the color will stand, and more pressure might be used. Some form of finishing might easily be resorted to. I have recently seen sole leather, essentially mineral tanned, stand a 12-inch column of water for more than three weeks because it had been treated with a small percentage of grease, the use of which was not perceptible in the sample. The leather when in suitable condition might be treated with oils and greases in some judicious way, either directly, or by the application of emulsions, sulphonated oils or spirituous solutions, or even by the formation of suitable metallic soaps. Or hard waxes could be rolled in in the final rolling, and brushed up into a more brilliant finish than is at present given. All these methods are easy to apply to particular cases, and would help considerably in waterproofing a leather.

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A certain standard of waterproof quality is thus within the reach of every tanner, and only such leather as could pass certain fixed tests should be used for official purposes. There should be plenty of incentive to the enterprising tanner to do this. Mineral sole has been advertised and boomed as waterproof in the public press, and is making headway because a certain public has been educated into asking for it.

If the boot maker would only take his courage into his hands he could influence matters greatly. A determined member who would make up his mind to sell a pure, waterproof, vegetable-tanned sole boot would probably get it, and steps could be taken by which the tanner might be induced to brand such leather with some sort of recognized stamp. The age of vegetable tannage is still flourishing, and will probably continue to flourish if the quality of the leather is looked after, but the advantages of mineral tannages, which research is rapidly improving, must not be overlooked.

Since writing the above the author has had conclusive confirmation of the fact that the English leathers A and O are not representative of English tannages, but had only been rapidly tanned to meet the demand for leather caused by war conditions. He has seen the results of over 50 analyses of British leathers made immediately before the war; most of these show less than 23 per cent. of soluble matter, very few exceed 25 per cent. and none exceed 30 per cent. A very small proportion only is adulterated with Epsom salts, glucose or both. The results of these analyses may be published at some future date.

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## JAPANESE WHITE LEATHER.*

*By Max Ray.*

As far as the writer knows after an experience of about twenty-five years in the leather trade, no white leather has been produced in the Western Hemisphere similar to the Japanese white hides with which many people in all parts of the world are acquainted, although perhaps unknowingly in most cases. This class of leather is probably the toughest in existence and is, therefore, largely used for brace or suspender ends or tabs and occasionally for all leather braces, its substance being ideal for the purpose.

The reason why no attempt has been made to imitate this unique leather is probably to be found in the fact that, before the Japanese-Russian war, the price of Japanese white hides was so remarkably low that American or European tanners could not possibly compete against the native product; in fact, the raw material was then dearer in Europe than the finished leather in Japan. Of course, raw hides from the Orient are not nearly as good in quality as the American or European; they are comparatively thin and poor. Perhaps the most important factor in the low price of Japanese raw hides, however, was the backward state of the native leather industry which, indeed, has only made progress on modern lines during the last few years. Previously, leather-making was considered to be work only suitable for men of the lowest caste.

At all events, the cost of Japanese white hides was so low that more than one experiment was made in Europe in redressing them, and it would have been a paying proposition had the experiments been successful. One result of the investigations, however, was to show that the white hides were not leather at all, strictly speaking, but were merely cured. They certainly look and handle like leather, but are of no use for boots, or any purpose where they would be exposed to moisture, as they become "pelty" when wet. The most likely reason why the hides cannot be redressed satisfactorily is that the skins are not limed and are afterwards finished by an oxidation process.

However that may be, the ancient art of making Japanese

* *Shoe and Leather Reporter*, Nov. 18, 1915.

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white leather presents certain features of practical interest of which the chief is the remarkable preservation of the natural strength of the raw hide. It is commonly supposed that after they are unhaired, the hides are simply placed in a river which has a natural bedrock of alum, which converts them into leather. This may be true to a certain extent and would then easily account for the low cost of production, but it is pretty certain that this process alone would not suffice to produce such a satisfactory leather as that which finds its way to the European and American markets.

From a Japanese leather manufacturer the writer learned the following details of the process as carried out, at any rate, in one part of Japan. The raw hides to be treated are soaked in the river for 3 to 4 days in summer, and for 11 to 12 days in winter or, in both cases, until such time as the hair becomes loosened. The hair is then scraped off with a blunt knife and the hides are thoroughly washed and fleshed. They are now ready for dressing.

The hides are placed in a tub or vat of water to which about 1¾ liters or kilograms or 3¾ pounds of common salt per hide has been added. The hides are then treaded with the bare feet for several hours, after which they are left in the tub for one or two days. When the salt seems to be fairly well taken up, the hides are dried in the sun. The whole of these initial processes of dressing are repeated, after which the hides are softened and soaked preparatory to oiling them. Rape seed oil is spread over the flesh side, using from 20 to 30 nomme (75 to 112½ grams or 2¾ to 4 ounces) per hide and the hides are stocked.

They are then alternately exposed to the sun and softened, the operations being repeated two or three times when the leather is in what is known as the half-bleached condition.

From this stage the treatment varies according to climatic conditions. Warm and sunny weather naturally hastens the process. In summer the hides are first bleached for six hours and then piled up for three or four days, these operations being repeated several times before the tannage is completed, which in favorable weather, takes about a month. In the winter, however,

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the period for bleaching is from ten to fifteen days, and the hides are laid in pile for a longer time than they are in the summer, from six to seven days being the usual period. The tannage is not generally completed under three months in the winter.

Finally, the hides are again put into the river to remove surplus salt, and are then exposed to the sun until dry when they should be perfectly white and ready for measuring and packing.

The leather looks very much like ordinary tawed leather but it certainly has quite different characteristics from the American and European alum and salt dressed leathers. Perhaps the most striking feature is the difference in the toughness of the two kinds of leather, the Japanese being incomparably stronger. In other respects it is inferior, that is to say, it has not such a good appearance and "feel" as the ordinary tawed leather. Still, it is particularly useful for one or two purposes and its peculiar properties merit a few theoretical observations.

The first point to be noted is that the hair is loosened by simply placing the hides for a few days in a river. Apparently the process of putrefaction is relied upon, as the much longer time taken in the winter seems to indicate. If the river bed contained alum, however, the slipping of the hair would be much retarded and it would seem to be preferable to use the sweating process in a warm room or cellar. The dressing is even more puzzling for it is not generally considered that salt of itself can make flexible leather. Professor Meunier, of the Tannery School at Lyons, has shown, however, that dehydrating salts have the power of isolating the fibers of skins and converting them into supple, if somewhat empty, leather. His theory may apply to the making of Japanese white leather; but, in any case, the process seems to merit scientific investigation.

Again, what part, if any, does the subsequent light dressing of oil play? Rape seed oil undoubtedly has a tanning effect and effectually combines with the fibers of the hide for no trace of it is seen in the finished leather. But it is doubtful whether the small quantity used can materially aid in the formation of leather. The more probable assumption is that only sufficient is used to keep the leather supple and prevents its drying stiff. Besides, if too much oil were applied, the leather would be quite unsuitable

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for its most important purpose, namely, for brace ends or tabs, which must be dry and show no signs of grease.

It is obvious that the frequent exposure of the hides to the sun plays an important part. It would assist the salt to withdraw the moisture from the interior of the hide, and would aid the bleaching properties of the salt. The making of the leather must depend largely on the processes of dehydration and oxidation.

Although the process is a primitive one, it opens up complicated theories which would be worth a thorough examination. Its simplicity in practice is attractive but its utility is limited. Beyond its usual applications the only important industry for which it might be useful is glove making. It would be a remarkably cheap dressing for glove leather, especially with the aid of up-to-date machinery, but some method of softening the leather would have to be devised.

In reviewing the process, practical men would not be satisfied, without seeing the process throughout, that good leather could be made by the use of salt alone. They would probably look for the key to the tannage or tawing in the contents of the river. On this point the writer has no data but if the river did contain sulphates of aluminum and potassium in solution, the process would naturally follow the ordinary lines of tawing. But if this be so, how is it that the leather is so much stronger than the average tawed leather?

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## A SIMPLE METHOD OF OBTAINING MELTING POINTS OF FATS, ETC.*

*By Arthur W. Knapp, B.Sc., F.I.C.*

In this method the substance is placed on the bulb of the thermometer. The thermometer is inserted in a corked test tube, which acts as an air bath, and the test tube is placed in a beaker of water or glycerin. The liquid should be boiled and cooled to prevent the formation of bubbles on the side of the beaker.

*For Fats, Waxes, or Fatty Acids.*—Very fine scrapings are taken with the point of a knife over a representative surface of the material. These fine scrapings are transferred with as little

* *J. S. C. I.* Nov, 30. 1915.

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injury as possible to the bulb of the thermometer. They should cover less than one-half of the bulb. Under these conditions one can plainly see when the sharp outline of the scrapings begins to soften, and also when the fat is completely transparent.

*For Crystalline Organic Substances.*—If the bulb of the thermometer be pushed into a powdered organic substance some of the powder adheres. A very faint film, or a few crystals is all that is necessary. The powder reflects irregularly the light coming from the mirror surface of the bulb, and the point at which the substance becomes liquid is plainly seen. A crystalline substance which does not adhere should be first powdered.

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## NOTE ON THE DETERMINATION OF TANNIN.*

*By D. B. Dott, F.I.C.*

The method at present in vogue for the determination of tannin consists in ascertaining the amount of matter which is absorbed by hide-powder from an infusion of the tanning material. Though the absorbed matter consists mainly of tannic acid, the weight is known to be increased by other constituents of the infusion. The hide-powder method is open to the theoretical objection that it does not follow that everything absorbed by hide can fairly be called tannin; on the other hand, a metallic precipitation process is obviously open to the objection that other compounds besides gallotannic acid may be present which give insoluble precipitates with metallic oxides, and there is apt to be some uncertainty as to the composition of the precipitate. On the whole, the preference for the hide-absorption process would be justified provided it were capable of giving constant results. That an unvarying percentage of tannin is not easily obtained by different operators on the same sample, is evident from all the literature on the subject. It seems to have been the object of much patient research to lay down a series of elaborate instructions, by following which it is hoped that uniform results maybe attained.[1] J. H. Yocum (*J. S. C. I.*, 1897, 16, 419) states

* *J. S. C. I.*, Nov. 30, 1915.

[1] [Editors Note. Our readers will observe that the references given in this paper refer to a period some years before the shake method had been brought to its present form. The author's remarks about a factor for tannin show that a metallic precipitate method is valueless for unknown solutions.]

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that "the hide-powder should be freed from readily soluble substances by washing immediately before adding to the tannin solution, a correction being made for the dilution caused by the adhering water. A mechanical means of shaking completes the tanning operation before there is time for the production of more soluble hide. The adoption of 20° as the temperature of filtration removes a source of error. It is of great importance that uniform quantities of hide and solutions of uniform density be employed in the estimations. The most serious cause of discordance is that different preparations of hide-powder do not give the same result." By the Leeds Conference of I. A. L. T. C. (*J. S. C. I.*, 1903, 22, 114) it is intimated: "The hide powder must not contain less than 11.5 per cent. of nitrogen. The amount of soluble hide substance must not exceed 5 milligrams per 50 cc. of solution. A correction must be made for the tannin absorbed by the filter paper. It is advisable to discard the first 150 cc. in filtering the liquor, and the filter ought to be kept as full as possible during filtration." Under the heading of "Non-tannins" we are informed: "this should be conducted by the filter method till next Conference, but members may use the chromed hide method of the Association of Official Agricultural Chemists, if it is stated in the report that the A. O. A. C. method has been substituted for the I. A. L. T. C. method." J. R. Mardick (*J. S. C. I.*, 1904, 23, 1187) points out that other matters in considerable quantity are absorbed by hide besides tannin, especially when a large excess of hide powder is used, as in the approved method. This is specially true of the prepared extracts which are now largely used. The weight of leather obtained in actual working shows that the tannin is always over-estimated. The maceration method gives uniformly about 1 per cent. less than the official method. Mardick recommends that the hide powder should be more highly chromed, in order to make it less liable to yield soluble matter to the tannin infusion, in the process of estimation. R. Lepetit (*J. S. C. I.*, 1910, 29, 1170) states that the shake method has not given results so nearly agreeing with the old filter-bell method as, on its adoption as the official method, it was stated to do. A concordance to within 1-1½ per cent. of tannin between the two methods was claimed, while, as a matter of fact, differences of 4, 5, and 6 per cent. have been found in estimating tanning materials

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by the two methods. Lepetit suggests precipitation by ammoniacal zinc acetate as a preferable method for tannin determination. That it is hoped to attain constancy of result by minute attention to detail, and by every chemist conducting the operations in precisely the same way, is evident from the following quotation from the well-known handbook of Clowes and Coleman. "The whole is agitated for fifteen minutes in a corked bottle, which is caused to rotate not less than 60 revolutions per minute, and the contents are then squeezed immediately through linen, stirred, and filtered through a folded filter of sufficient size to hold the whole filtrate. The evaporations are rapidly carried to dryness at steam temperature in flat-bottomed porcelain, Jena glass, or platinum basins of not less than 6.5 centimeters diameter, and the residue is dried at 98°-100° *in vacuo,* or in a water or steam oven with small compartments until it is of constant weight: it is subsequently cooled in a small air-tight desiccator over dry calcium chloride for at least twenty minutes. Not more than two basins are to be placed in one desiccator, and the basins must not be wiped after removal from the desiccator. The basins must be weighed rapidly to avoid absorption of moisture. The moist hide powder should not be kept for more than a few hours before it is used, without special precautions." Having occasion to estimate a sample of sumac, I followed the above and a number of other directions with reasonable closeness, with the result that I obtained 22.8 per cent. tannin. An experienced assistant, using the same hide powder, obtained 23.7 per cent. On repeating the determination I obtained 23.3 per cent., as the highest of three experiments. The sample was passed on to a very capable analyst, but one who had confessedly no experience of the "shake" method of analysis. He reported 21.0 per cent. We were afterwards informed that the proper expert figure for the same sumac was 25.6 per cent.

One is impelled to the opinion that this so-called official method for estimating tanning materials, is an exceedingly empirical and eminently unsatisfactory analytical method. A good process ought to yield substantially the same result in the hands of different analysts, if these give the matter ordinary care and intelligent treatment. Of methods for tannin determination, other than

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by the use of hide, nearly all depend on precipitation of the tannic acid by a metallic oxide. This may be effected either by adding a solution of an appropriate salt to an infusion of the tanning material, or by digesting the infusion with excess of metallic oxide. Yellow oxide of mercury has been used in the latter manner with apparent success. I have only experience of the use of a hot solution of cupric acetate, which is added in excess to the warm infusion, the mixture heated to boiling, the precipitate being collected on a filter and washed with hot water. After drying it is ignited, treated with nitric acid, dried, and again ignited. The weight of CuO is multiplied by 1.305 to obtain the equivalent of tannin. By this means it is easy to obtain practically constant results. In a few comparative experiments, the copper results were from 1 to 2 per cent. below the rather variable hide powder figures. But this raises the question whether 1.305 is really the correct factor by which the weight of CuO should be multiplied. This would be a useful subject of investigation. 0.367 gram of tannic acid (as used in medicine), dried at 100°, was dissolved and precipitated by copper acetate as above described; 0.623 gram of dry precipitate was obtained, which gave on ignition 0.252 gram CuO. This would seem to indicate 1.45 as the factor for gallotannic acid, which if accepted would bring the figures for sumac nearer those found by the hide process. I am not certain how the factor 1.305 was originally derived, but in a paper by Maltscheffsky on determination of tannin in tea, for which purpose he uses a standard solution of cupric acetate containing 7.657 grams of CuO to the liter, and 1 cc. is said to be equivalent to 0.01 gram of tannin. These figures correspond to the factor 1.305. The tannin of tea is known to be different from that of galls and sumac. According to Hilger and Tretzel the tannin of tea has the composition and properties of an anhydride of digallic acid, gallotannic acid being essentially digallic acid, although sometimes associated with glucogallic acid and possibly other compounds in small proportion. Even although a varying factor had to be employed in the estimation of different kinds of tanning materials, the method would possess the great advantage of comparative constancy for the same sample. Different chemists would get the same result with the same thing. It seems to me that the absorption by hide should

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rather be used as a check on the percentage indicated by metallic oxide, while the latter is the more exact method on which to base analytical data. If there were any reason to suspect the presence of a non-tannin which gives a precipitate in a slightly acid solution of the metallic salt, the hide powder treatment might also be employed as a useful means of confirming the result or helping to detect adulteration. It may appear audacious to suggest the setting aside or relegating to a secondary place of a method which has received so much attention, and on which so much discussion has been bestowed; but I think that what has been written by others, as well as results that have come under my own notice, indicate that a change in the standard method of estimating tanning materials is much to be desired. I have no doubt that chemists who devote themselves more especially to that kind of work, are capable of devising a better process, and that the successful solution of the problem will lie in the direction of chemical reactions, and not in the absorptive properties of skin.

### Discussion.

Prof. Walker said it was well known that absorption phenomena were much less easily reproducible than ordinary precipitations, and probably one could get much more concordant results in the hands of different chemists with the method of precipitation by metallic salts than by the hide-powder method; but of course the problem remained to adjust the two methods to correspond with each other. No official method, which gave different results in the hands of different well-trained chemists, could be said to be satisfactory.

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## ABSTRACTS.

**A Gravimetric Method of Estimating the Tannic Acid Content of Tanning Materials.** A. Gawalowski. *Ledertechnische Ruudschau*, Nov. 18, 1915, Vol. 7, No. 46, pp. 337-8. In contrast to the earlier method of Fleck, Sackur, Wolff and Hager, the author does not precipitate the materials from their water solution by means of basic copper acetate, but first extracts the material with alcohol and ether, which brings the tannin and resins, but not pectin, into solution. An aliquot part of the alcohol-ether solution is evaporated at about 40° C. and the residue dissolved in cold water, thus separating the resinous matter. An aliquot part of the aqueous filtrate is now precipitated with verdigris solution and the brown

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precipitate collected on a rapid-working filter which has been weighed after drying to constant weight. The precipitate is air-dried in a warm place, and then taken to constant weight on a water bath, and its weight found. The filter is now burned in a current of air or oxygen in a suitable tube, until the copper is all converted into oxide. Hydrogen is then passed through the tube to reduce the oxide to metallic copper, which is weighed. The difference between this weight and that of the precipitate is called the combustible matter. This value for combustible, calculated to a percentage of the original material, gives the tannin content, and may be found either directly as above, or figured (by means of a factor previously determined) from the weight of copper oxide. To figure tannin from this precipitate by the equation $1.304 \times CuO = \text{tannin}$, as suggested by Hager, has been found undependable. The use of a copper-factor is also impossible, as according to the author's determinations this factor varies from 1.24 in the case of sumac to 2.52 for nut-galls, valonia, oak bark and morin (fustic?), being about 1.42 for myrobalans and quercitron and 1.95 for oak-wood extract. Hager's method can therefore be of value only when the material to be examined is in its natural condition. In all other cases the above described method would seem necessary. The method is as follows: Of barks take 50 grams, or of the very rich materials 15 grams. Grind moderately fine. Place the 50 grams of ground bark in a ½-liter flask with 250 cc. of a mixture of 1 of alcohol to 2 of ether. Fit a good cork coated with tinfoil. Digest at room temperature at least one day. To a 15-gram sample use 150 cc. of alcohol-ether. Remove 10 cc. of the clear solution to a porcelain dish and evaporate. Take up the residue with 50 cc. of cold water and filter. Precipitate 25 cc. of the filtrate with verdigris solution, and proceed as before described to weigh and burn and reduce the precipitate. The "combustible" found corresponds (for a 50-gram sample) to 1 gram of material, or for a 15-gram sample to 0.5 gram of the original substance. Concentrated extracts may be analyzed by shaking 10 grams with 200 cc. of alcohol-ether. The copper oxide factors for various materials are given in the table, which shows what percentage of the copper tannate is CuO.

| | | | |
|---|---|---|---|
| Valonia | 34–38 | Knoppern | 35 |
| Pine bark | 10–15 | Myrobalans | 35–42 |
| Oak bark | 34–39 | Sumac | 40–50 |
| Oakwood extract | 26–33 | Quercitron | 44 |
| Nut-galls | 34–40 | Morin (fustic?) | 26–38 |

L. B.

**Concrete Shoes.** ANON. *Concrete-Cement Age*, p. 110, 1915 (through *Chemical Abstracts*). Cement is used for weighting, waterproofing and strengthening sole leather. Ordinary sole leather is soaked in water until pliant, allowed to become half dry and given a coat of boiled linseed oil on the grain side. A bath is prepared of cement 8 ounces, borax 2 ounces and cold water to consistency of milk. To each pound of leather, ½

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pound of this mixture is allowed. The soaking lasts 24 hours, when it is dried and oiled with linseed oil. The durability is increased 100 to 200 per cent.

**Disinfection of Hides in Argentina.** *S. and L. Rep.*, Dec. 2. 1915. Under date of Sept. 14, 1915, the Consul General of the United States in Argentina, Mr. W. Henry Robertson, issued a circular letter to the exporters of hides, directing their attention to the regulations in regard to the disinfection of hides intended for exportation to the United States. These regulations specify that the hides shall be immersed in a solution of mercury bichloride, 1 : 1,000, or a 5 per cent. solution of carbolic acid. The methods which had been in use at Argentine ports involved sprinkling or wetting the hides, sometimes on the lighters and sometimes on the decks or in the holds of vessels. The letter of the Consul General further stated that unless the regulations were complied with he would be obliged to refuse to certify invoices and issue the disinfection certificates. To this letter a committee representing the exporters of hides made a lengthy reply, citing the stringent regulations in force in Argentina in regard to infectious diseases of cattle as a reason for permitting Argentine hides to be exported to the United States without requiring disinfection by immersion. It appears that such disinfection is not required in the case of hides from Mexico, Australia, New Zealand, Great Britain or Scandinavia unless infection is known to exist at the time in the district from which the hides come. The Argentine exporters argue that in consideration of the great care exercised by the Argentine Government in regard to care and inspection of cattle and quarantine of infected districts the same privileges ought to be accorded to Argentine which are given to the other countries named. They also observe that the additional cost of disinfection, which they estimate at nearly 4 per cent. of the value of the hides, would fall on the American purchasers and thus place them at a disadvantage in comparison with their European competitors. They also remark that Argentine beef is now admitted to the United States on certificate from the Argentine authorities, and it seems inconsistent to impose upon the by-products of the cattle industry restrictions from which the principal product is free. The committee offers the suggestion that the regulations of the United States Government in regard to disinfection of hides be altered so as to read as follows:

> A certificate signed by the American Consular Office for the district from which the hides were shipped showing disinfection by one of the methods hereinafter described will be required upon the entry of all hides of neat cattle which have not been subjected to a process of tanning including calfskins and hide cuttings or parings or glue stock, with the following exceptions, which exceptions will not be made, however, in case of importations from districts where anthrax is prevalent.
>
> 1. Hides, whether wet or dry, the product of, and imported from any part of North America or of the Argentine Republic.

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This statement is dated at Buenos Aires, September 28th, and signed by the following gentlemen: V. Vilamil, of V. Vilamil & Co.; E. K. Hoyt, Argentine representative of the Central Leather Co.; W. D. Little, Argentine representative of Kistler, Lesh & Co.; S. D. Allchin, of S. D. Allchin & Co.

**The Tannins of the Oak Tree.** ANONYMOUS, in the *Shoe and Leather Reporter* of Nov. 18, 1915. Oak bark is the oldest source of tannin, and still perhaps the most widely used. Oak wood also furnishes tannin, which is chiefly used in the form of extract. The fruit of the oak tree, the acorn cup, is one of the richest of tanning materials, that known as valonia being especially valuable. Tannin is also contained in the excrescences found on oak trees caused by the attack of insects and known as oak-galls. These "gall nuts" furnish perhaps the purest form of tannin found in nature. Certain species of oaks contain tannin in the roots and root-bark. Oak wood from different parts of the tree contains different percentages of tannin, the base having more than the top, and heart wood more than sapwood. Leather tanned with oak bark has enjoyed such high repute that it is now common to find brands of leather in the making of which little or no oak bark has been used marked "pure oak bark tanned." Oak bark tannage owes its reputation partly to the excellence of the material and partly to the method of tanning used when oak bark was the only material employed. At that time weak liquors were used, and the time required was very long. The leather produced in this way had a much smaller percentage of water soluble matter than that made now with stronger liquors and in a shorter time. The modern leather is less water-proof and has less actual leather substance in a given weight of leather. Chemically speaking, the bark contains two sorts of tannin, both catechol and and pyrogallol. To the presence of these two kinds of tannin it is perhaps due that oak bark is applicable to the tannage of so many different kinds of leather, both light and heavy. The percentage of tannin in oak bark varies between 8 and 15, bark from the base of the tree being richer in tannin than that from the top. The old method of use was to strew the ground bark between the hides in the layaway pits, leaving them in these layers for long periods. The partly spent material was then leached, and the liquors so obtained were used in the early stages of tanning. The insoluble material deposited in oak liquors on standing, called bloom, is also deposited in the fiber of the leather during the slow process of tanning formerly used. This bloom gave to the old-time leather much of its firmness and wearing quality. The methods of extraction formerly used were very wasteful. Extraction was carried out at ordinary atmospheric temperatures, by which process only 60 or 70 per cent. of the tannin extractable at 80° C. was extracted. If 80° C. is exceeded in extracting oak bark, a part of the tannin is destroyed, and more coloring matter is extracted from the bark. The tannin of oak bark is sold almost entirely in the bark, while that of oak wood is found

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in the market in the form of extract. The wood contains about 6 or 7 per cent. of tannin. The extract resembles chestnut wood extract, and the liquors made from it decompose easily.

## DIED.

At his home in Brooklyn, N. Y., on the afternoon of December 23rd, Cassius W. Norris, in the forty-first year of his age.

The above announcement will bring deep regret and sorrow to the members of our Association and to many of us a feeling of great personal loss. By his death we are deprived of one of the most valued workers in the particular field of our activities.

To one whose privilege it was to glimpse beneath the reticence so characteristic of the man, there appears nothing more dominant in his nature than his integrity. Above all things did he value honesty, and measured to this standard he lived his life. And his work was a reflection of his character, painstaking and sincere always.

Mr. Norris held a degree from State College, Pennsylvania, and after his college course, worked in the Experiment Station of that institution. He then accepted a position with the firm of Albert Trostle and Sons, Milwaukee, Wisconsin, where he remained for four years, leaving to become chemist for A. Klipstein and Company, and continuing in this capacity with the Argan Tannin Company. In June, 1914, he formed a partnership with H. C. Reed under the name of the Reed-Norris Laboratory, which partnership continued up to the time of his death. He was Vice-President of our Association for the terms of 1905-6 and 1913-14 and Member of the Council for the terms of 1907-8 and 1908-9.

Perhaps the most admirable traits of Norris' character were displayed in the battle he was called upon to wage against the illness that finally conquered him. For somewhat more than a year he fought, suffering greatly, yet through it all, with courage undaunted, held fast to faith of ultimate recovery. At times it would seem that he might win, giving courage to us of lesser faith than his. Uncomplaining, ever optomistic, he resisted thus stubbornly unto the very end. May we not say:

O death, where is thy sting?
O grave, where is thy victory?

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## WATER PENETRATION APPARATUS FOR LEATHER.

*By C. T. Gayley.*

Leather chemists are using various forms of apparatus for determining the comparative resistance of leather to water penetration. No standard type has been developed. The water pressure used by different workers varies from that of a water column from 15 to 30 inches high, to 40 pounds pressure. High pressure does not seem advisable, as the time for penetration is so short as to make accurate comparison difficult. On the other hand, the small pressure exerted by a 2-foot water column makes conditions quite similar to those in actual wearing, where the time of penetration is shortened by the bending of the sole when one steps.

In sole leather tests, the practical value of the determination is undoubtedly limited by the fact that we are unable to duplicate actual wearing conditions. The comparative value remains great, and is especially useful in examining sole, belting, harness and upper leather. For curried belting leather and water-proof belting, the water penetration time gives us an exact idea of the water resisting value of the materials used for stuffing. The same may be said of treated harness, sole and upper leathers.

The late Dr. Kilp, a former member of the A. L. C. A., designed a water penetration apparatus which has given such good service and results in this laboratory, that we are tempted to describe it, hoping the description may be of interest and use to fellow workers.

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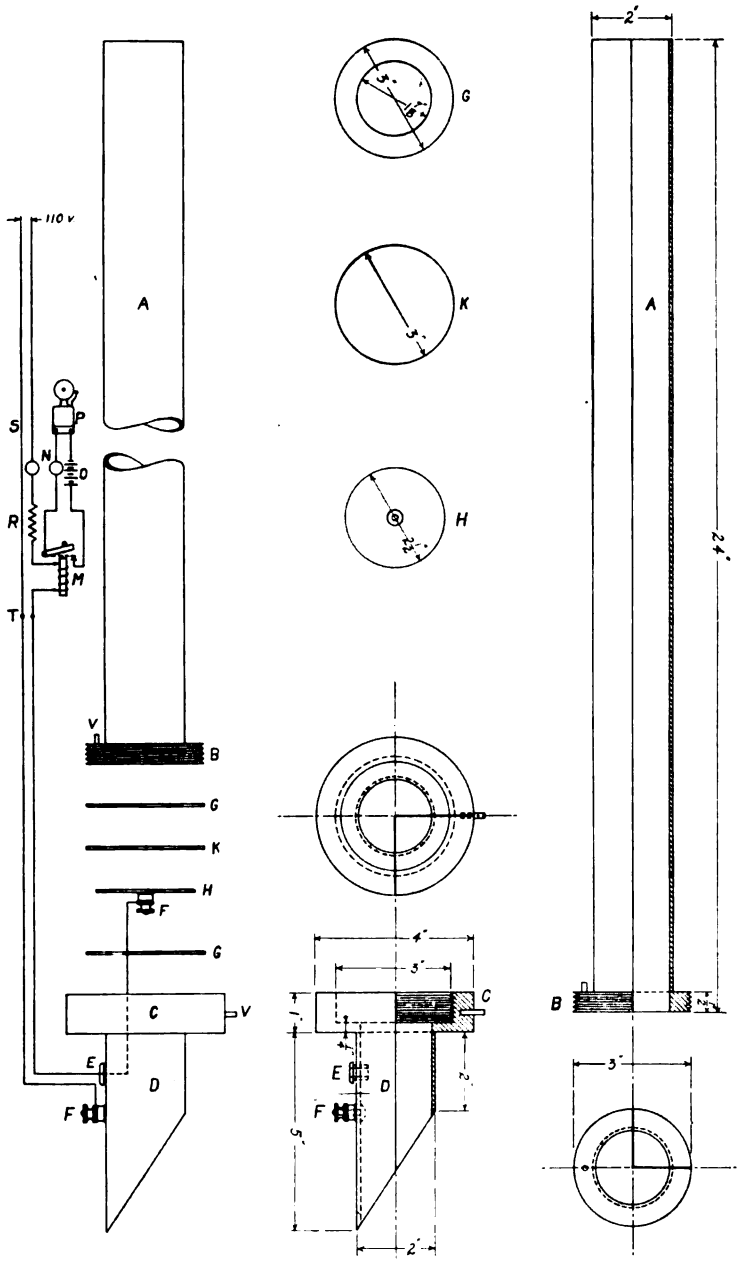


FIG. 1.

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The apparatus consists essentially of two parts, the timing device and the penetration apparatus.

Fig. 1 gives in detail the construction of the penetration apparatus. At the left is shown the manner of assembling when a test is to be made. A rubber gasket *G* is first placed in the flange *C*, and then the copper disc *H* is placed in the center of the gasket. The insulated wire connection attached to *H* by means of the binding post is brought out through the rubber bushing *E*, as indicated. Then the disc *K*, of the leather to be tested, is placed upon the copper disc, another rubber gasket *G'* is placed over it and finally the collar *B* is screwed tightly into the flange *C*, clamping all firmly together. The gaskets serve to make the joints water-tight above, and to insulate the copper disc below. The tube is now clamped upright on a ring stand, and when the entire apparatus is ready, the upper part of the tube is filled with water to within ½ inch of the top; the water level is to be made the same each time to insure a constant pressure on the leather.

The timing device consists essentially of a $1.00 alarm clock, two dry cells, an electric bell, two snap switches, one constant ringing drop and a resistance. These are connected in such a way that when water penetrates the leather clamped in the cylinder, the constant ringing drop falls, the bell rings and the clock stops.

When away from the laboratory the bell may be turned off by means of the right-hand switch, since if the bell were allowed to ring for some time, the dry cells would be exhausted unnecessarily. The apparatus is attached to a 110-volt lighting circuit or in case such a circuit is not available two gravity cells connected in series may be substituted, in which case the resistance may be dispensed with.

Referring to the reproduced photograph, the die for cutting out the leather discs may be seen in the foreground, while one of the wrenches with which the leather is clamped tightly in the penetration tube may be seen lying on the base of the ring stand.

For comparative work it is necessary to have the pressure and the thickness of the leather constant. Since samples of leather cannot be had of uniform thickness, Mr. Riethof suggests that all results be corrected to a thickness of 5 millimeters. Thus if the average thickness of the leather is 4 millimeters, and the

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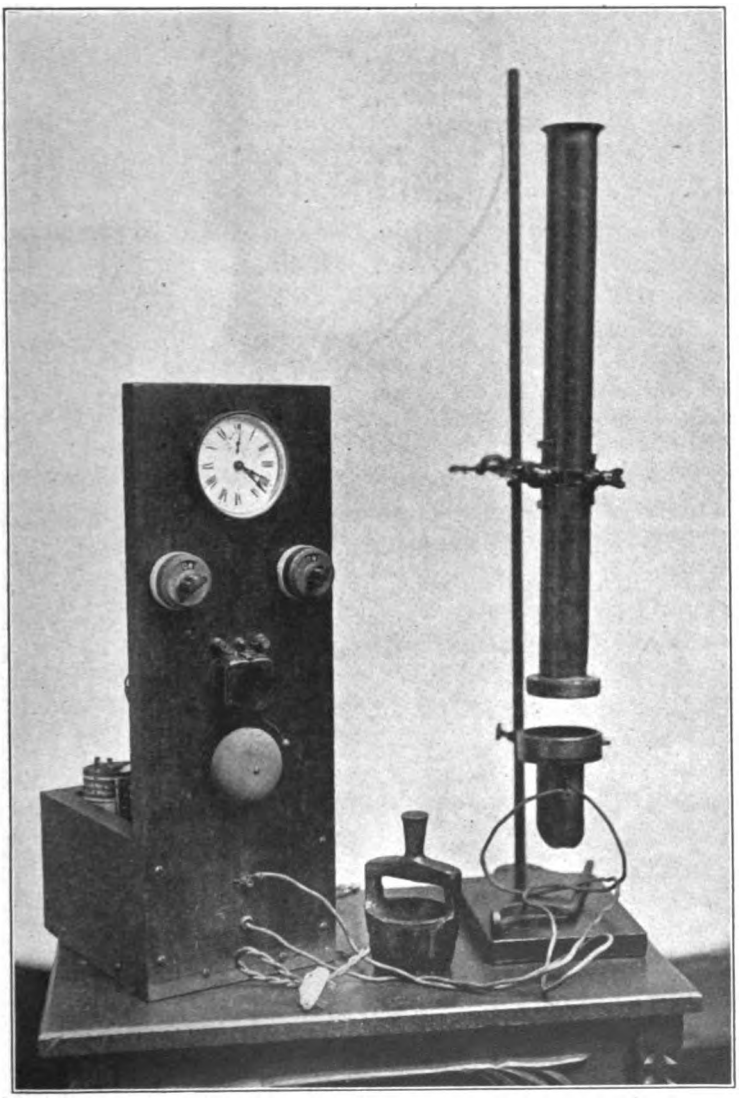

FIG. 2.

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time of penetration is ten hours, the time corrected to 5 millimeters thickness would be:

$$\frac{\text{time} \times 5}{\text{thickness}} = \frac{10 \times 5}{4} = 12.5 \text{ hours.}$$

However, insofar as practicable, samples of leather should be chosen that are approximately 5 millimeters thick, making conditions in every respect as uniform as possible.

Another factor that enters into comparative work is the sampling of the leather. Samples taken from back, shoulder and belly of the same side show considerable variation in the time required for penetration. The following results illustrate this:

| | Back | Shoulder | Belly |
|---|---|---|---|
| Union sole leather A. | 5 hrs. 25 min. | 5 hrs. 57 min. | 5 hrs. 50 min. |
| Union sole leather B. | 5 hrs. 30 min. | 5 hrs. 33 min. | 2 hrs. 41 min. |
| Hemlock sole leather (bull) .... ..... | 12 hrs. | 12 hrs. 56 min. | 12 hrs. 49 min. |

It follows that in reporting results, the part of the hide from which the sample was taken should be mentioned.

Allowing a margin for profit, the apparatus as described above may be made for $25.00. To any who are interested, the author can furnish complete constructional details or will aid him in securing the complete apparatus.

WM. F. MOSSER CO. CHEM. LABORATORY,
Richwood, W. Va.

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# THE CHEMISTRY OF THE SKIN.*

*By Arnold Seymour-Jones.*

[The following paper was written by the late Arnold Seymour-Jones about 1910 or 1911, probably as an address to the Leeds University Students' Scientific Society, and though, no doubt, the author might have further added to it had he lived, it contains much valuable information not to be found in text-books, and is well worth publication for its own sake, as well as a memorial of one from whom we hoped much.

Mr. F. C. Thompson and the writer have carefully gone through and corrected the small verbal errors of the typewritten manuscript, but further changes have not been needed, though one or two signed notes have been added.—H. R. PROCTER.]

There is probably no more obscure and complicated branch of science than physiological chemistry, and not the least complicated question of that branch is the chemistry of the skin. I must, therefore, apologize for my temerity in approaching such an obscure subject, but I hold that there is no question more interesting and more vitally important to chemists in general, and "leather trades' chemists" in particular than the chemistry of the proteids, and particularly of a subdivision of that group—the albuminoids. My aim, therefore, in writing this paper is to bring together, insofar as I can within the limits of one paper, the opinions of the world's leading authorities past and present, on this matter, and so obtain a brief consensus of opinion as to the probable chemical constitution of the skin. As this paper will be written from the point of view of applied chemistry of leather manufacture, technical terms will be introduced from time to time, but will be fully explained as they occur.

To the superficial observer the skins of the various species of mammalia appear entirely different from one another. On closer observation, however, it will be found that not only are the skins of the higher animals so alike that a description of one species will almost equally apply to another, but also that the lower animals, *e. g.*, lizards, alligators, etc., possess the same characteristics, with of course substantial modifications in the structure of the epidermis, and the arrangement of the fiber bundles. The

* *Collegium*, London Edition, Nov. 1915, pp. 288-304.

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fact is frequently overlooked that the skin, besides being a covering for the animal, has also to act as an organ of sense and secretion. It is consequently complicated in structure, and it will be necessary before tackling the purely chemical aspects to briefly study the general anatomy of the skin. This anatomical outline will only be so far extended as to illustrate the difference in chemical constitution between the various layers.

The skins of all higher mammalia may be roughly divided into two layers:—

1. An outer layer, or epidermis (epithelium).
2. An inner layer or corium (true skin).

These are not only totally different in functions, but in origin. "In the ovum of a higher animal the living germ consists of a single cell, which, as soon as fertilized begins to multiply by repeated division. The mass of cells thus formed early differentiate into three distinct layers, from the upper of which the epithelium arises, while the true skin, together with the bones and cartilage, is derived from the middle one."* This is fundamentally important as the true skin, bones, and cartilage resemble one another very closely chemically, while the epidermis is entirely different.

The epidermis, or epithelial layer, is responsible for the origin, growth, and development of all the horny substances of the body, *viz.*:—hair, horns, hoofs, claws, nails, the sudoriferous and sebaceous glands, hair sheaths, etc., etc. These substances with slight modifications due to inorganic salts, are chemically identical with the epidermis. The latter consists of living cells, whose life appears to begin on the inside, next to the true skin, from which they obtain their nourishment. During the course of their existence they are forced outward by the birth of new cells, and as they become further and further removed from their food supply become flat and thin, and finally die of starvation, being rubbed off the outside as dead scales of skin. Thus we have young cells in the inner half of the epidermis, and adult cells in the outer half. This clearly differentiates two layers, *viz.*:—an outer, older portion—the epidermis proper, and an inner, younger portion, known as the *"rete malpighi."*

The boundary between the epidermis and the corium is very

* Procter's Principles of Leather Manufacture.

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clearly defined, by an exceedingly fine membrane, known as the "hyaline," or glassy layer. This layer is interesting chemically, as it presents marked differences in constitution to the other two main layers.

The "Corium," or true skin is chiefly composed of the so-called "connective tissue fibers." These are interlacing bundles of white fibers, which are composed of fibrils of extreme fineness, cemented together by a substance somewhat more soluble than the fibers themselves (Procter). The fiber bundles become loosely woven in the center of the corium, and consequently a large number of fat-cells are formed in the interstices. This is especially observable in the case of sheepskins, and the fats, besides presenting other interesting chemical aspects, appear to have a solvent action on the surrounding fibers. Besides the connective tissue fibers, the corium contains a considerable number of fine yellow, elastic fibers and also blood and lymph, which latter supply its nourishment. These all differ chemically from the corium.

Below the corium we have the "panniculus adiposus," which is connective tissue uniting the skin and the body. It is similar in chemical constitution to the connective tissue fibers of the corium.

This completes our anatomical survey of the skin, and we must now turn to the chemical consideration. The skin is built up chiefly of albuminoids. The epidermis consists mainly of keratins, while the corium, or true skin is largely collagen, the so-called "glue-yielding tissue." Elastin is found in the yellow elastic fibers, and some of the blood vessels of the corium. The walls of the blood and lymph vessels are keratinous, while the vessels themselves contain soluble albumins, and globulins.

The constitution of the "hyalin" of the hyaline layer is exceptional, and also an extremely difficult question, presenting interesting aspects which will be discussed later.

Chemically albuminoids are albumins, as they behave in all ways exactly as the albumins. They form substitution products, they ferment, or may be hydrolyzed by acids or alkalies into albumoses, peptones, and amino-acids; they form salts, and have the same percentage composition, and give the same color reactions as do other albumins. The difference between the two classes is apparently mainly physical and anatomical. Physically,

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of course, they possess the property of great firmness, as one of their functions is to form supporting and covering structures for the body. The formation of the shells of the molluscs is an interesting example of this firmness, as the shells are only modified skins. Their extraordinary hardness and rigidity is due to albuminoids forming an organic ground-matrix, which subsequently becomes impregnated with mineral matter. This goes on to a certain extent in the epidermis of the higher animals, as phosphates and aluminates are secreted in the keratin of the latter. It also seems probable that the hardness of the skins of the elephant, hippopotamus, etc., is due to secreted mineral matter.

Dr. Cohnheim, of Heidelberg, laid down a rule that "the essential feature of all connective tissues is that they must be completely insoluble in all animal juices." This has raised considerable opposition, and Mann, in his book on the Proteids, says that he has ample evidence to prove that during inanition the connective tissues all over the body, including the bones (also the skin) are diminished, and are partly converted into "circulating proteid." Whether this be so, or not, it is quite certain that the juices and fats of the body do penetrate into the corium, and seem to have some solvent action on the corium, and especially on the forementioned middle-layer. They seem unable to diffuse to any great extent through the hyaline layer, although it is from the corium that the epidermis obtains its nourishment. That in cases of starvation nature should endeavor to support life by allowing the subject to live upon its own tissues seems not only probable, but self-evident, and the extraordinary tenderness of the bones and skin of an invalid, during chronic, or particularly severe illness, appears to be a case in point. It is noteworthy, however, that the albuminoids do not form part of the cell, but are structures which have been secreted by the cells—the latter becoming included in the secretions during the formation of the supporting tissue.

As we have previously noted the epidermis, or epithelial layer consists mainly of keratin. The latter has also been recognized in hair, nails, hoofs, horns, feathers, etc. It is found in the egg-shells of birds, and of the *echidna aculeata* (a mammal) of crocodiles and snails, in the cocoons of leeches, and in many other tissues among the invertebrates (Mann). Keratin is notable as

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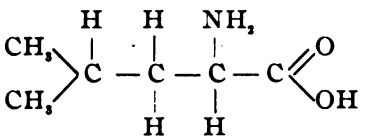
the most insoluble albuminoid. Although the analyses of pure keratin differ greatly with the experimenter, one and all agree in attributing to it a very high sulphur content. Among its hydrolysis products are the following:

| | Per cent. | | Per cent. |
|---|---|---|---|
| Glycocoll | 0.34 | Cystin | 6.8 |
| Alanin | 1.2 | Serin | 5.7 |
| Leucin | 18.3 | Tyrosin | 4.58 |
| Phenylalanin | 3.0 | Arginin | 2.25 |
| Pyrrolidin carboxylic acid | 3.6 | Tryptophane | trace. |
| Glutaminic acid | 14.0 | Ammonia | much. |
| Aspartic acid | 2.5 | Amino-valerianic acid | 5.7 |

It is probably to cystin that keratin owes its high percentage of sulphur, but other sulphur-containing hydrolysis products have been found, including sulphureted hydrogen and methyl mercaptan, and it appears improbable that these are obtained from the hydrolysis of a cystin molecule (Kossel). From the above table it will be seen that leucin, cystin, and glutaminic acid are the main constituents.

Leucin $C_6H_{13}NO_2$ is one of the most important and general of the amino-acids, and was consequently one of the first to be isolated. It is iso-butyl α-amino-acetic acid.



It has been found in all albumens, and this characteristic of wide distribution is shared by α-pyrrolidin carboxylic acid, alanin, phenylalanin, and glutaminic and aspartic acids. Consequently it may be supposed that these acids form the base of the keratin molecule. Leucin is soluble in 46 parts water. There are three varieties, *viz.*:—dextro-rotatory, lævo-rotatory, and racemized leucin. The melting point of all three is 293–295° C., and they decompose on melting. Leucin has a naturally occurring isomer, iso-leucin which is always found with leucin, and is consequently present in keratin. Iso-leucin is α-amino-caproic acid, and it is possibly due to this acid and its derivatives that we have the strong goaty smell when hide substance is undergoing decomposition. Caproic, caprylic, and capric acids are said to be also

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present. It has been noticed by Fischer, Müller, Kossel, and others that leucin bears a direct relationship to the carbohydrates in many of its reactions. This is strenuously opposed by Cohnheim and Halsey, but as the case is still *sub judice* we merely comment in passing, and await interesting developments.

Cystin occurs in two distinct forms, *viz.*:—α-cystin or protein-cystin, and β-cystin, or stone-cystin, but as only the former is known to occur in keratin we will confine ourselves to a description of its properties. α-cystin, or to fully describe it, di-(β-thio-α-aminopropionic acid) has the following structural formula:

$$\begin{array}{l} S.CH_2 - CH.NH_2 - COOH \\ | \\ S.CH_2 - CH.NH_2 - COOH \end{array}$$

α-cystin has no melting point, but decomposes between 252–261° C. When heated with HCl under pressure it gives rise to alanin, and $H_2S$ and $NH_3$. On treating this with nitrous acid it is converted into δ-lactic acid, which is identical with the sarco-lactic acid found in muscle during *rigor mortis*, and during life in the tissues of the body. As carbohydrates also readily pass into lactic acid, alanin acts as a link between them and cystin (Mann). Thus we have our second connecting link between keratin, and the carbohydrates.

Glutaminic acid is α-amino-glutaric acid, and does not possess many points of interest with regard to the skin; for, while it is present in such quantity as to leave no doubt as to its leavening effect on keratin, the study of its properties has not been carried to such a pitch as to permit of an obvious explanation of any of the phenomena apparent to the leather manufacturer.

Tyrosin, tryptophane, and phenyl-alanin are the representatives of the aromatic series in keratin. Serin, α-amino-β-hydroxy-propionic acid is also present in considerable quantities, and is nearly related to cystin, as the latter is thio-serin. E. Fischer suspects some relationship to the carbohydrates here, serin being a simple hydroxy-amino acid, and regards glucosamine as a link between the hydroxy-amino acids and the hexoses. Amino-valerianic acid, the only other important constituent is so like leucin in properties that it is difficult to isolate in the presence of the latter.

Having studied the properties of the main substances which go to build up the keratin molecule, we shall now endeavor to study

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the properties of the keratin of the epidermis, and to reconcile the latter with the former. Pure keratin obtained from the epidermis is quite insoluble in water and dilute acids. Digestive ferments only render it soluble after some time, and with great difficulty, and the act of bringing keratin into solution decomposes it. The question of the solubility of keratin is an extremely important one, and one on which there are widely differing opinions.

In the process of leather manufacture, before the skin can be tanned the whole epidermis from the surface to the hyaline layer has to be removed, and is practically of no value. This is as a rule accomplished by soaking the skins in milk of lime, and occasionally by the use of caustic alkalies, or alkaline sulphides. The whole epidermis is removed in anything from ten days to three weeks, depending on the class of skin and season of the year. The question of the solvent power of the sulphides for keratin is slightly different from that of the caustic alkalies and lime, and will be considered later. It has been definitely proved that only the dissolved lime has any action on the skin, and a saturated solution of calcium hydroxide at ordinary temperatures is less than N/20. Also the solutions of caustic alkalies used never exceed 0.1 to 0.15 per cent., this solution being found to be more effective than one of greater strength. It is commonly accepted among "applied" chemists that the epidermis and hair are soluble in lime liquors. Professor Procter in his "Principles" says that "Keratin is dissolved by caustic alkalies; the epidermis and softer horny tissue are easily attacked, while the hair and horn require strong solutions, and the aid of heat to effect complete solution. The caustic alkaline earths act in the same manner as the alkaline solutions; hence, lime easily attacks the epidermis and loosens the hair, but does not readily destroy the latter."

Against this we must put the view of Smith,* states that even 10 per cent. KOH only dissolves keratin with the aid of heat, and in the cold a 20 per cent. caustic soda solution is required to render it soluble, while the digestive enzymes only accomplish the same slowly. This view is supported by Kühne and Chittenden in the same Journal, and endorsed by Mann in his book on the proteids, but I believe Professor Procter maintains on physico-chemical grounds that a dilute solution of a caustic

* *Zeitschrift fur wissenschaftliche Zoologie*, Vol. 19, p. 469.

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alkali has more solvent power than one of the order of 10 per cent. say. Be this as it may, pure science says that it is impossible for keratin to be soluble in dilute caustic alkali and lime solutions, while applied science says that it actually is accomplished by lime solutions whose strength cannot exceed N/20. How are we to reconcile these two diametrically opposite views? In my humble opinion we can only take the one loop-hole left to us, and presuppose the existence of bacteria and digestive ferments in the depilatory solution. According to Mann, and other observers, adult keratin differs chemically from young keratin. Obviously this is of importance, as we have stated in the anatomical introduction, the life of the epidermis cell begins against the hyaline layer, in the *rete malpighi,* and finishes on the surface as dead skin. Thus the *rete malpighi* is built up of young keratin, while the outer layer consists of adult and dying keratin. As has been noted digestive ferments have great difficulty in rendering adult keratin soluble, but young keratin is readily dissolved by pepsin. Now, I have noted on many occasions that the lime solution appears to attack firstly the lower layer, the *rete malpighi,* and so enable the upper layer to come away in quite large fragile sheets, by reason of its being detached from the skin. It is also well known in the leather trade that old lime liquors are nearly always highly bacterial, and in primitive tanyards the use of bacterial water and lime liquor is still fairly common. These facts obviously fit in with both theories.

The lime liquors are always prepared in old lime pits, and a fresh lot of skins are nearly always started in the oldest lime liquor. It appears evident then, that the lime liquors must contain digestive ferments due to bacterial action. These are able to attack the young keratin of the "*rete malpighi,*" and so detach the epidermis from the true skin. Another fact in support of this theory is that a new lime liquor made up in perfectly clean vessels has no depilatory action, until suitable exposure to air has given it an opportunity of becoming bacterial. In laboratory and other experiments it is frequently the custom to add small quantities of old lime liquors to new ones, in order to make the latter unhair, and dissolve the epidermis. This is of course the same thing as inoculating the new limes. There appears to be an increasing tendency in the leather trade to paint the depilatory

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solution or paste on the "flesh" or inner side of the skin. By this device the paste rapidly penetrates through the corium, and the young keratin of the hair roots and *rete malpighi* is the first to be reached and dissolved, rapid depilation thus taking place.

It is interesting to note that a process of liming was invented a few years ago, which involved the precipitation of calcium hydroxide in the skin, by first immersing the skin in a dilute solution of caustic soda, and then, after suitable treatment, passing it into a calcium chloride solution. The notable point about this, in favor of our theory, was that no depilatory action could be obtained, the hair or wool of the animal being as uniformly set and perfectly intact at the end as at the beginning of the process. To remedy this, a soaking in "bacterial" was suggested. Therefore, there seems a strong case in favor of the view that no depilation can be obtained with lime water and caustic alkalies without the intervention of bacteria and bacterial ferments.

The action of the alkaline sulphides on keratin appears to have been completely overlooked by pure scientists, but Procter, the representative of applied science, states definitely:—"Alkaline sulphides on the other hand seem to attack the harder tissues with at least the same facility as the soft ones, the hair being often completely disintegrated, while the epidermis is still almost intact; hence their applicability to unhairing by destruction of the hair." Among the sulphides and sulphydrates used are:—realgar, or red sulphide of arsenic, crystalline sodium sulphide, and calcium sulphydrate; but ordinary crystalline sodium sulphide is the one commonly used. Its action on keratin is supposed to be due to its hydrolysis in solution into sodium hydrate, and sodium sulphydrate.

$$Na_2S + H_2O = NaOH + NaSH$$

What the peculiar function of the sulphydrate-ion is in dissolving keratin is unknown, but it is certain that these sulphides have a most corrosive action on the epidermis and hair, and even on the collagen of the corium to a certain extent. The question is very obscure, and its solution lies probably in the regions of physical chemistry.

From the principal chemical constituents of keratin, it appears evident that keratin is allied in some subtle way to the carbohy-

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drates. The epidermis of the skin in some of its reactions seems very like a severely modified carbohydrate, but none has ever been obtained from keratin by hydrolysis, or otherwise. An especially noticeable feature about keratin and the epidermis is the large amount of ammonia evolved when hydrolysis takes place. This is especially noticeable during the later stages of the aforementioned "liming" process in a leather works. Such quantities of it have been obtained that its recovery has been suggested.

The epidermis gives the following reactions of a typical albumen:

1. *An Intense Millon's Reaction.*—Blackish red coloration with a solution of mercurous nitrate in nitric acid. This shows the presence of tyrosin.

2. *An Intense Xanthoproteic Test.*—The addition of a strong solution of nitric acid produces a yellow color, which on the addition of ammonia solution becomes a vivid orange color, or on the addition of a soda solution a reddish brown.

3. *A Strong Lead Sulphide Test.*—If the epidermis be boiled with a lead salt and soda solution a brownish black precipitate is formed.

The epidermis only contains keratin proper, and does not contain neuro-keratin, gorgonin, and iodo-keratin, which are all of the class of keratins. The question of inorganic salts in the epidermis is of some importance in tanning, but their presence only affects the physical properties of the skin. The same salts are present in the corium.

Having dealt with the structure of the epidermis at some length we must now pass on to consider the chemistry of the hyaline layer. It is extremely difficult to know where to put this substance, or mixture of substances, in our classification. Krukenberg has described a number of substances related to "hyalin," which he found amongst the lower animals, and which he thinks are intermediate between albumins and carbohydrates.

A compound known as "chitin," which was formerly classed among albuminoids, has been shown to be a nitrogenous carbohydrate, a derivative of glucosamine. Mann suggests that "hyalin" might be a mixture of carbohydrates formed by splitting off from the glyco-proteids. Whatever may be its constitution,

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the hyaline layer is extremely tough and resistant. It is practically unaffected by acids, alkalies, and digestive ferments. It is capable of taking a high polish, and it forms the polished surface of most of the leather to be seen, omitting those leathers with a "nap" in which it is removed, and those "patent" leathers in which it is covered up.

We now come to the most important layer of the skin, the corium or true skin. It has been generally accepted in applied science circles that the white fibers which form the major portion of the corium are identical with gelatin, and Procter in his book says that "the white fibers of the corium (or true skin) are either identical with gelatine, or only differ from it in their molecular condition or degree of hydration." Though they cannot be considered identical with gelatin, the ease with which these fibers yield gelatin seems to point to the fact that the latter is the first derivative of the former. These fibers are, therefore, composed of a substance allied to gelatin which has received the name of collagen. Any attempts to bring the latter into solution result in the formation of gelatin, consequently little is known about the constitution of the "glue-yielding tissue." Pepsin easily attacks the ordinary connective tissue fibers in the presence of hydrochloric acid, but trypsin does not. Connective tissue may therefore be obtained in the pure state by removing the other albuminous bodies present with trypsin.*

Hofmeister regards collagen as an anhydride of gelatin and has obtaind a substance which he believes to be identical with collagen by heating gelatin until it loses water. Gelatin on being heated to 130° C. becomes absolutely insoluble in water even at boiling temperature. Professor Procter notes that collagen is certainly less easily soluble in hot water than ordinary gelatin. Hofmeister says that the conversion of collagen into gelatin depends on hydrolysis. One important physical difference is that the former always exists as a fibrous structure while pure gelatin exhibits no fibers. It is evident, however, that gelatin is a sufficiently direct derivative of collagen for a study of its chemical properties to reveal most of those of the latter.

Pure dry gelatin is a colorless amorphous powder, but the commercial gelatin occurs in the shape of glassy plates, which contain

* Trypsin is the active ferment of Röhm's Oropon. H. R. P.

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water. From the very early times of organic chemistry gelatin has invited research, but the early analyses were performed by scientific dilettanti, and do not agree at all. This was probably due to their inability to prepare gelatin in the pure condition, as other tissue constituents were present, including collagen fibrils, etc. Various observers have tried to overcome this difficulty by treating white fibrous tissue with dilute alkalies and trypsin, which do not attack collagen, but the transition from collagen to gelatin and its hydrolysis products is so easy that the final products may very well differ from one another.

A recent and active investigator of gelatin is W. S. Sadikoff, and he has shown "that it is at present impossible to prepare glutins, which are chemically pure, and which agree with one another in all their properties." This does not, however, interfere with the investigation of the hydrolysis products of gelatin and its general structure, but is very evident in the analytical figures and in studying the reactions. A typical analysis of pure gelatin is according to Sadikoff:—Carbon 50.9 per cent., hydrogen 6.8 per cent., nitrogen 17.97 per cent., sulphur 0.53 per cent. It will thus be seen that while the percentage of nitrogen is large, the amount of carbon is relatively small, and by reason of this low figure gelatine possesses a low heat value, which according to Stohmann is 500-700 calories less than that of most other albuminous substances. The history of the evolution of the study of the hydrolysis products of gelatin is an interesting one, but is too lengthy to be dealt with here.

Gelatin is extremely rich in glycocoll, and Emil Fischer estimates the amount at 16.5 per cent. The complete list of dissociation products is as follows:

| | Per cent. | | Per cent. |
|---|---|---|---|
| Glycocoll | 16.5 | Aspartic acid | 0.56 |
| Alanin | 0.8 | Oxy-pyrrolidin-carboxylic acid | 3.0 |
| Leucin | 2.1 | Lysin | 5.6 |
| Phenylalanin α-pyrrolidin Carboxylic acid | 0.4 5.2 | Histidin | 0.4 |
| Glutaminic acid | 14.0 | Arginin | 9.3 |
| | | Ammonia | 0.43 |

Serin—trace.

It will be seen that the principal constituents are glycocoll, glutaminic acid, pyrrolidin- and oxypyrrolidin-carboxylic acids,

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and also arginin and lysin, two of the hexone bases. The third hexone base, histidin is very feebly represented. Of the three possible aromatic compounds, only phenylalanin is present, and that only in a small amount. The figure given for phenylalanin is by Emil Fischer, but the analyses of Spiro, Dureschi, Maly, Nencki, and Selitrenny show a considerably higher percentage. Pure gelatin does not give a Millon's reaction, thus showing the absence of tyrosin.

Glycocoll, the simplest of the amino-acids is too well known to require description. The principal properties of interest are, firstly the typical property of all amino-acids, that of acting both as a base and an acid; secondly it can be determined quantitatively more accurately than any other mono-amino acid; thirdly, it is only contained in the anti-group of albumins, and hence is absent in most proteids; fourthly, on oxidation, *e. g.*, with chromic acid it gives rise to prussic acid. This is also a property of gelatin. This last fact is of special interest to leather manufacturers, as the so-called "poisonous nature" of chrome leather may be due to the cyanides formed in the leather.* It is also noteworthy that of all oxidizing agents chromic acid produces the most. The mean percentage of prussic acid produced by chrome from gelatin is 2.75 per cent., but from glycocoll as much as 11.10 per cent. has been obtained by Aders Plimmer.

The mechanism of the formation of HCN from glycocoll, according to Mann, takes place in two reactions, nitro-acetic acid is first formed by the oxidation, and this on being heated to 120° C. breaks down into prussic acid, carbonic acid, and water.

$$NH_2CH_2 - CO.OH + O_2 = NOH.CH - CO.OH + H_2O$$
$$NOH.CH - CO.OH + \text{heat} = HCN + CO_2 + H_2O$$

Prussic acid is also formed by the oxidation of many other amino-acids, but the only other which gives it in any quantity is aspartic acid, and the mechanism of the reaction is as yet unexplained.

*** This hardly seems possible, since prussic acid is very volatile and soluble, and no chromic acid should remain unreduced in a modern chrome-leather. H. R. P.**

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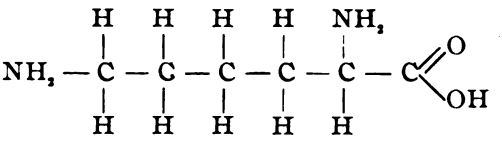
Two of the hexone bases are present in gelatin in considerable quantities.—

Lysin is α-ε-diamino-normal-caproic acid.



It is said to be the mother substance of pentamethylene diamine or cadaverine $CH_2—NH_2$

$(CH_2)_3$

$CH_2.NH_2$

This seems a point worth noting for the basis of a possible method for the titration of hide substance dissolved in lime or other putrescible liquors. A point of interest is that it has an insoluble picrate, which is probably part of the mechanism of those experimental tannages with picric acid, by which quite good leather has been obtained. Another point of interest is that according to certain authorities the nitrogen determination by Kjeldahl's method does not always give correct values, probably because a part of the nitrogen is converted into hydrocyanic acid by oxidation, and so lost for titration purposes. Especially is this so in the presence of a permanganate. As permanganate is often added to assist the oxidation of leather in a Kjeldahl analysis, this may possibly be a source of error. Zickgraf has obtained considerable quantities of hydrocyanic acid by oxidizing lysin with a permanganate. By oxidizing gelatin with potassium permanganate and caustic potash, Maly obtained the oxy-proto-sulphonic acids, which are interesting from a synthetical point of view.

The mechanism of the dissociation of gelatin has to a small extent been revealed by Kutscher, Zickgraf, and Schenek. On oxidizing gelatin by permanganates, especially calcium permanganate in boiling solution, they obtained oxaluramide or oxalan, and ammonium oxaminate was also observed. Ehrmann suggests that hydrolysis takes place as oxamide ⇌ oxaminic acid ⇌ oxalic acid and ammonia.

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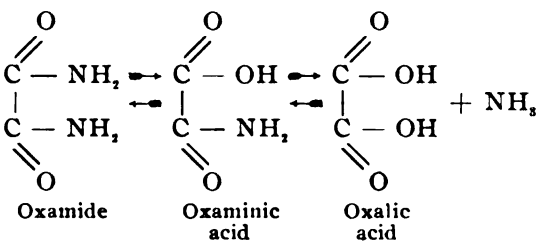
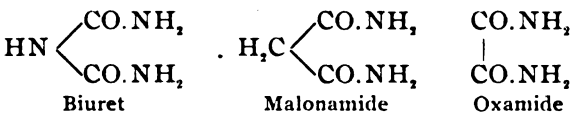



The question as to whether oxamide is actually contained as such in the gelatin, or whether it is formed secondarily out of the ammonia, and the hydrocyanic acid set free by the oxidation of the gelatin is still an open question. Kutscher and Schenek incline to the former view, and state that the biuret action given by gelatin may be due to it, in part at least, as the reaction is believed by Schiff to be given by all compounds of the following types:




where two $CO.NH_2$ groups are linked either to a carbon or nitrogen atom or to one another. On the oxidation of gelatin Seemann found oxalan, and calcium and ammonium oxalates, and in addition the following ether soluble acids:—oxalic, succinic, benzoic, formic, acetic, and butyric acids, also benzaldehyde, and perhaps also propionic and valerianic acids.

Nasse and Framm found that heating gelatin under pressure for four days mainly produced albumoses. Paal concludes that on dissociation the gelatin molecule is resolved with the assimilation of water into peptone molecules of gradually decreasing molecular weight until a point is reached at which the peptonization ceases, and the simpler peptones are resolved into amino-acids, lysin, lysatin, etc.

Gelatin belongs exclusively to the anti-group of the albumin molecule. Prolonged tryptic digestion gives no crystalline products, but only albumoses and peptones. Both peptic and tryptic digestion are very slow. It has been noticed that the first derivatives of gelatin are the gelatoses. These lose glycocoll and become peptones. Then these peptone molecules become resolved into molecules of decreasing molecular weight until pep-

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tonization ceases, and as mentioned before the simple peptones break down into amino-acids, etc. The only sulphur-containing decomposition product yet obtained is sulphureted hydrogen. Gelatin gives a well marked violet biuret reaction, but many of the qualitative reactions, which should be absent, are given faintly, owing probably to the presence of foreign substances.

A very interesting portion of the study of gelatin is the question of the substances with which unhydrolyzed gelatin will or will not give a precipitate. This is especially interesting to the scientific leather manufacturer, as if a compound has the power of rendering gelatin insoluble and imputrescible, it will in all probability make leather out of hide fiber. Mann notes that gelatin is precipitated by the chlorides of gold and platinum, and stannous chloride, but these precipitates are soluble at boiling temperatures, reappearing on cooling. This property is also shared by mercuric chloride in the presence of hydrochloric acid or neutral salts. Basic lead acetate and mercuric nitrate give precipitates. The alkaloids are also good precipitants for gelatin. An interesting but complicated precipitate is the one caused by phospho-molybdic acid which becomes permanent on heating. The most important precipitates, however, are those formed by tannic and chromic acids, which are said to be dissolved by heating, and return on cooling.

Procter in his book discusses the question of gelatin precipitation with tannins very fully. This forms an interesting parallel to the views of pure scientists quoted above, and the description is so thorough that I venture to quote *in extenso*:—

> "Gelatin is precipitated by all tannins, even from dilute solutions; one containing only 0.2 gram per liter is rendered distinctly turbid by gallo-tannic acid, or infusion of gall nuts, but some other tannins give a less sensitive reaction. The precipitate is soluble to a considerable extent in excess of gelatin, so that in using the latter as a test for traces of tannin, care must be taken to add a very small quantity only. The addition of a little alum renders the reaction more delicate. Whether the precipitate is a definite chemical compound has been disputed, as its composition varies according to whether gelatin or tannin be in excess. Böttinger states

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that the precipitate produced by adding gelatin to excess of gallo-tannic acid contains 10.7 per cent. nitrogen, indicating the presence of 66 per cent. of gelatin on the assumption that gelatin contains 16.5 per cent. nitrogen. Digested with water at 130° C., the precipitate is decomposed yielding a solution which precipitates tannin, and probably indicating the formation of a more acid compound. Gelatin with excess of oak bark tannin gives a precipitate containing 9.5 per cent. of nitrogen corresponding to 57.5 per cent. gelatin."

It will thus be seen that the constitution of the precipitate is very variable even with the same tannin.

Mann states that with tannic acid salt-free gelatin gives no precipitate, and this is borne out by Weiske, who has shown that bone-gelatin, which is identical with that of the skin, is not precipitated by tannin until a trace of sodium chloride is added. Precipitates are also obtained with iron, aluminium, and titanium salts, bromine and chlorine water, and potassium iodide solution. On heating a solution containing gelatin and formaldehyde an insoluble "formo-gelatin" is produced. A technical chemist of some repute advanced the theory that gelatin had four bonds. Two of these bonds could be satisfied by vegetable tanning solutions, and a third by mineral tanning solutions, etc. Needless to say, the idea broke down on examination. The question of the substance which cements the fibrils of the connective tissue is one of great interest, and it has been studied by Reimer.

Lime and baryta solutions possess the property of splitting up the fibers of the corium, and forming smaller and smaller fibrils, at the same time dissolving the cementing substance. This substance is recovered from solution by neutralization with acetic acid, when it is thrown down as a flocculent precipitate, and is known as coriin, and fresh lots can be obtained from the same piece of skin *ad infinitum*, or until the skin has practically disappeared. Reimer's analysis of coriin was as follows:

| | Per cent. | | Per cent. |
|---|---|---|---|
| Carbon | 45.91 | Hydrogen | 6.57 |
| Nitrogen | 17.82 | Oxygen | 29.60 |

Procter believes that in all probability coriin is merely an impure degradation product of hide fiber.

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None of the more modern "star" investigators in organic chemistry have ventured on a formula of any sort for gelatin. Hofmeister, Blennard, Schützenberger, and Bourgois, agree on the formula $C_{76}H_{124}N_{24}O_{29}$ and from this formula Professor Procter* calculates the percentage composition as follows:

| | | Per cent. |
|---|---|---|
| $C_{76}$ | 912 | = 49.7 |
| $H_{124}$ | 124 | = 6.8 |
| $N_{24}$ | 336 | = 18.3 |
| $O_{29}$ | 464 | = 25.2 |
| | 1,836 | |

Professor Paal has endeavored to determine the molecular weight of gelatin from cryosopic and boiling point methods, and arrives at the value 900. In the light of modern investigation this value is probably too small.

On dry distillation gelatin gives a mixture of pyrrol and pyrridin bases. Solutions of acids and caustic alkalies have the remarkable property of violently swelling gelatin, causing it to absorb water. Professor Procter has studied the question exhaustively, and has testified to its great complexity. He believes that actual chemical combination does actually take place to some extent. It will be readily observed that the amino-groups of the gelatin can combine with acids, and the carboxyls with alkalies and bases. The swelling, however, is wholly attributed to water, in consequence of the increased facilities given to the hide-fiber, by the acids and alkalies, for its absorption. It is interesting to note that the sulphuric acid of a decinormal solution can be completely removed by hide, leaving only water without a trace of acid recognizable by litmus. The acid or alkali absorbed by the skin cannot be removed in any reasonable time by washing with water, but is generally completely removed by neutralization. Procter's experiments have led him to the conclusion that one gram of air-dried gelatin will combine with about 0.025 gram of actual HCl when placed in a very dilute solution of the latter,

* Procter (*Trans. Ch. Soc.*, 1914, p. 313.) has derived the formula $C_{35}H_{57}O_{13}N_{11} = 839$ from physical considerations. This gives $C_1$ 50.06 per cent., $H_1$ 6.79 per cent. $O_1$ 24.79 per cent., $N_1$ 18.36 per cent. This refers to the smallest possible molecule, which is probably usually polymerized. H. R. P.

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and this compound will absorb 40–45 grams of water while still in the state of jelly. Maximum swelling is obtained with dilute solutions. The question of the physical explanation of this does not come within the scope of this paper.

The next point of interest in the corium is the structure of the elastic fibers, which are the yellow fibers of the skin. They rival keratin in stability and insolubility, and were optically isolated by Stirling in 1871 while working in Ludwig's laboratory. He digested the skin with artificial gastric juice, which rendered everything indistinct, with the exception of the nerves, the nuclei, and the yellow fibers. These fibers are now known to be distinct chemically from either gelatin or keratin, and consist of the individual albuminoid elastin. Elastin is widely distributed in the animal kingdom, and is hardly more soluble than keratin. It is not attacked by 5 per cent. potassium hydroxide solution in the cold, and hardly by hot 1 per cent. potassium hydroxide solution. The digestive ferments, trypsin and pepsin, and hydrochloric acid, slowly decompose it forming albumoses. To obtain it in a pure form the other constituents of tissue with which it occurs are removed by alternate treatment with acids and alkalies. The following typical analysis of elastin is by Chittenden and Hart.

| | Per cent. | | Per cent. |
|---|---|---|---|
| Carbon | 54.08 | Hydrogen | 7.2 |
| Nitrogen | 16.85 | Sulphur | 0.3 |

A characteristic of elastin is its high carbon, and low sulphur content. An analysis by two of Emil Fischer's pupils gave the following figures for the hydrolysis of elastin.

| | Per cent. | | Per cent. |
|---|---|---|---|
| Glycocoll | 25.75 | α-pyrrolidin-carboxylic acid | 1.74 |
| Leucin | 21.38 | Amino-valerianic acid | 1.0 |
| Alanin | 6.58 | Glutaminic acid | 0.76 |
| Phenylalanin | 3.89 | Aspartic acid | ? |

Horbaczewski found 0.7 per cent. ammonia, and 0.25 per cent. tyrosin. Schwarz obtained 0.34 per cent. tyrosin, and Kossel and Kutscher 0.3 per cent. arginin.

Mann notes that of all the albuminous substances, elastin is the poorest in tyrosin and arginin, and on subjecting elastin to bacterial digestion indol-derivatives are completely absent. Engel showed that elastin, which had been rendered soluble with alkali, gave all the color tests with the exception of the lead sulphide

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reaction. It is very questionable, however, if elastin can be dissolved without undergoing substantial alterations in structure, such as the change from collagen to gelatin. Barium peroxide renders the fibrils indigestible for pepsin, but more readily digestible for trypsin, while chromic acid in the presence of light has an exactly opposite effect.

The corium contains quantities of soluble albumins in the blood serum or lymph. The principal albumin present is serum-albumin itself, which formerly looked upon as a mixture, has now come to be regarded as a uniform and specific compound. Serum-albumin obtained from the blood of a horse has been crystallized, which supports Von Weimarn's view of the ultimate crystallization of all colloids. Hofmeister and Kurajeff from their analyses calculate the formula $C_{450}H_{720}N_{116}S_6O_{140}$ and the molecular weight as 10,166. The temperature of coagulation is 67° C. The dissociation products are the usual ones of an albumin, but glycocoll is absent. Leucin is the principal constituent and is present up to 30 per cent.; cystin is also present. There is also a globulin present, known as "serum-globulin." This has not been prepared in the crystalline form. In contradistinction to serum-albumin it has a high glycocoll content for an albumin (up to 3.52 per cent.). It contains 18.7 per cent. of leucin. Serum-globulin has been fractionized, and appears to be a collection of globulins, although it is at present impossible to say how many.

The remaining point of interest in the chemistry of the skin is the fat secreted amongst the loose fibers in the middle of the corium. The question has been studied by Mr. Alfred Seymour-Jones over a period of nearly thirty years. He finds that the amount of fat in the corium is directly due to the food of the animal. Consequently with the large increase of oil cake feeding, etc., the amount of fat is largely on the increase, much to the detriment of the skin for leather manufacturing purposes. This increase in fat is especially noticeable in sheepskins. Furthermore, Alfred Seymour-Jones has pointed out that the fat has considerable solvent power on the cementing substance of the connective tissue fibers, if not on the fibers themselves. This occurs in the center of the corium, and in some cases is so bad that the lower layer of the true skin is separated from the epi-

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dermis in sheepskins. This serious defect is known in practice as "looseness." The same observer notes that in many cases where this looseness is observed, hard nodules of fat are found just under the hyaline layer, in what he describes as "pepperbox formation." This formation has only appeared within the last few years since oil-cake feeding has become so general. The question of the solvent action of these fats is highly interesting, and requires further study. The fats are chiefly made up of the alcohols cholesterol and iso-cholesterol. They may be removed from the skin either by the use of a suitable solvent, such as benzine, or petrol ether, or by hydraulic pressure.

This completes our survey of the chemistry of the skin, and in closing I should like to apologize for the many imperfections of this paper, but I have tried faithfully to give the expressions of each authority while acknowledging the source. With the new methods of synthesis and quantitative analysis introduced by Fischer, Kossel, and others, it is probably not unreasonable to suppose that the synthesis of the albuminoids is fairly near at hand. A full comprehension of the gelatin molecule and its workings would go a long way to lighten the darkness which surrounds the scientific workers in the "mysterie and craft" of leather manufacture.

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## NOTES ON THE ANALYSIS OF ONE-BATH CHROME LIQUORS AND USE OF RESULTS IN THE REGULATION OF BASICITY.

*By Ernest Little, Instructor, Tanners' Institute.*

With the continued increase in the use of the one-bath chrome process, due to its cheapness and comparative ease in operation, the question of chemical control of this process becomes one of extreme importance. It is a fact that at the present time a very large number, if not a majority, of tanners using this process are doing so without the aid of chemical control. In some cases where control is kept the question might perhaps also be raised whether the results of analysis mean as much as they should to the chemist and consequently whether the tanner is deriving as much benefit as he should from the work.

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It is a well-known fact that the degree of hydrolysis of the chromic salt used in the one-bath method is one of the factors which determine whether or not a good tannage will be obtained. The normal or slightly hydrolyzed salts penetrate the stock quickly and uniformly but the effect can hardly be called a tannage because it is very light and can easily be washed out. The more basic salts, although they penetrate more slowly, give a much fuller and more permanent tannage. If, however, the hydrolysis has proceeded too far the surface of the stock will become coated with a highly hydrolyzed insoluble, chromic salt and a very brittle and unevenly tanned piece of leather results. The degree of hydrolysis which is best suited for the one-bath tannage is, perhaps, represented by the salts $Cr_2(OH)_2(SO_4)_2$ and $Cr_2(OH)_3Cl_3$. When these salts are used the tannage is not too slow; it is full, uniform and permanent.

Keeping in mind these facts, it is quite evident that the control chemist should have at his disposal a quick, accurate method of analysis for the one-bath liquor and should be able to use intelligently the results obtained. The following method of analysis has been tried out at Tanners' Institute and found to be quite satisfactory. A method of using the resultant data for the correction of the basicity of the bath is also given.

## Determination of Chromium in Chrome Liquor.

Ten cc. of liquor are measured into a 300 cc. Erlenmeyer flask and diluted to about 125 cc. with distilled $H_2O$. Three grams of $Na_2O_2$ are now added slowly and in small portions, shaking slightly after each addition. Boil about 30 minutes to destroy excess $Na_2O_2$. Dilute, if necessary, during boiling. Transfer, with careful rinsing to a 250 cc. ground glass stoppered iodine bottle. Cool to about 20° C.; add 8 cc. of concentrated HCl, 10 cc. of 10 per cent. KI solution. Shake thoroughly; allow solution to stand a couple of minutes and titrate the clear dark-red solution with N/10 $Na_2S_2O_3$, shaking constantly, until color changes to light yellowish brown. Now add about 1 cc. of 1 per cent. starch solution; dilute to about 200 cc. and slowly add $Na_2S_2O_3$ until the light green color of chromic salt appears.

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*Strength*

$$\frac{\text{Cc. N/10 } Na_2S_2O_3 \times 0.00173 \times 100}{10} \text{ or}$$

Cc. N/10 $Na_2S_2O_3 \times 0.0173$ = gram Cr. per 100 cc.

DETERMINATION OF CR. IN STOCK LIQUOR.

Ten cc. of stock liquor are pipetted into a 500 cc. graduated flask, made up to the mark with distilled $H_2O$ and thoroughly mixed. 25 cc. of this solution are then analyzed by the above method.

*Strength*

Cc. N/10 $Na_2S_2O_3 \times 0.00173 \times 200$ or cc. N/10 $Na_2S_2O_3 \times 0.346$ = gram Cr. per 100 cc. stock liquor.

NOTES.—Due to the varying strengths of $Na_2O_2$ the exact amount necessary for the oxidation can not always be definitely stated. It should be added in small portions until bluish green chromic salt has been completely oxidized to yellow $Na_2CrO_4$.

One-half hour boiling is usually sufficient to destroy the excess $Na_2O_2$. The analyst should not depend on any definite length of time for this operation, but the solution should be boiled until no more small bubbles of oxygen come off, the solution boils quietly and only the larger bubbles of water vapor escape. It is very important that the excess of peroxide should be destroyed, otherwise when the solution is acidified $Na_2CrO_4$ will be oxidized to the deep blue perchromic acid $HCrO_4$ and the analysis made worthless.

If, after adding the acid and KI, there are black specks of I floating on top, more KI should be added until the iodine is completely dissolved. If the solution at this point is still yellow, more concentrated HCl should be added until a sufficient amount is present to allow the complete reduction of the $H_2Cr_2O_7$.

After reaching what you consider the final end point with the N/10 $Na_2S_2O_3$ it is well to add a few drops of concentrated HCl, a little KI solution, and a small amount of starch solution. If the deep blue color reappears titrate again to the light blue color of chromic salt.

DETERMINATION OF BASICITY OF CHROME LIQUORS.

Pipette 10 cc. of liquor into a casserole and dilute to 150 cc.

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Heat solution to boiling, add 1 cc. of phenolphthalein (1 per cent. solution), run in N/10 NaOH, stirring constantly until the supernatant liquid above the precipitated $Cr(OH)_3$ shows a slight pink color.

*Strength*

Cc. N/10 NaOH × 0.0048 × 10 or cc. N/10 NaOH × 0.048 = gram $SO_4$ per 100 cc.

### Determination of Basicity of Stock Liquor.

Ten cc. of stock liquor are placed in a 500 cc. flask, made to the mark with water and mixed thoroughly. 25 cc. of this diluted solution are taken and analysis proceeded with as outlined above.

*Strength*

Cc. N/10 NaOH × 0.0048 × 200 or
Cc. N/10 NaOH × 0.96 = gram $SO_4$ per 100 cc.

Notes.—The volume must be sufficiently large to permit of the hydrolysis of the chromic salt to $Cr(OH)_3$ and $H_2SO_4$. This $H_2SO_4$ formed by hydrolysis is afterwards titrated for with the N/10 NaOH.

The solution must be kept near the boiling point, otherwise the NaOH will react with the precipitated $Cr(OH)_3$, dissolving it, and forming $Na_3CrO_3$. This action will not take place in very hot solutions, because, under these conditions, sodium chromite is hydrolyzed to $Cr(OH)_3$ and NaOH.

If aluminum is present in any but very small amounts it will interfere with this analysis. Not only will basic aluminum sulphate be hydrolyzed to $Al(OH)_3$ and $H_2SO_4$ which is neutralized by the NaOH, but unlike $Na_3CrO_3$, $Na_3AlO_3$ is not changed to $Al(OH)_3$ and NaOH by boiling. Therefore the NaOH will react with the precipitated $Al(OH)_3$ dissolving it and forming $Na_3AlO_3$. This can be corrected if the amount of aluminum present is known.

### Use of Above Results to Obtain Correct Basicity of One-Bath Chrome Liquor.

As has been stated it is, perhaps, agreed that the best salts for the one bath chrome tan are the basic salts $Cr_2(OH)_2(SO_4)_2$ or $Cr_2(OH)_3O_3$. Let us consider $Cr(OH)_2(SO_4)_2$.

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The ratio of Cr to $SO_4$ is 104 : 192 or 52 : 96. From the analysis of the bath determine the ratio of Cr. to $SO_4$ by the proportion $\frac{\text{grams Cr. in 100 cc.}}{\text{grams } SO_4 \text{ in 100 cc.}} = \frac{52}{x}$ ; $x$ = grams $SO_4$ combined with 52 grams of chromium.

If the ratio is above 96, too much acid is present and $Na_2CO_3$, $10H_2O$ must be added to bring the ratio down to 52 : 96. If the ratio is below 96, $H_2SO_4$ must be added to bring the ratio up to the standard.

Let us assume the analysis shows the ratio to be 52 : 99. When the ratio is 52:96, 1 gram Cr. $= \frac{96}{52}$ or 1.84 grams $SO_4$. When the ratio is 52:99, 1 gram Cr. $= \frac{99}{52}$ or 1.9 grams $SO_4$. 1.9 — 1.84 = 0.06 gram $SO_4$ to be neutralized for each gram of Cr present.

$$\overset{(98)}{H_2SO_4} + \overset{(286)}{Na_2CO_3\ 10\ H_2O} \rightarrowtail Na_2SO_4 + H_2O + CO_2 + 10\ H_2O$$

$\frac{Na_2CO_3\ 10\ H_2O\ (286)}{SO_4\quad (96)} = \frac{x}{1}$ ; $x = \frac{286 \times 1}{96}$ ; $x$ = 2.98 grams of $Na_2CO_3$, $10H_2O$ are necessary for every gram of $SO_4$ to be neutralized.

0.06 × 2.98 = 0.1788 gram $Na_2CO_3 10H_2O$ for each gram of Cr. present.

$$\frac{\text{grams Cr. in 100 cc.} \times \overset{\text{(cc. in gal.)}}{3785} \times 0.1788}{\underset{\text{(grams in lb.)}}{453.6} \times 100} = \text{lb. } Na_2CO_3\ 10\ H_2O$$

to be added per gallon.

*Summary.*

When there are more than 1.84 grams of $SO_4$ present for every gram of Cr, subtract 1.84 from this value and substitute the result in the follow equation

$$\frac{\text{grams Cr. in 100 cc.} \times 37.85 \times ?}{453.6} \text{ or}$$

grams Cr. in 100 cc. × 0.0834 × ? = pound $Na_2CO_3 10H_2O$ to be added per gallon to give the desired basicity.

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Let us assume the ratio to be below 96, *e. g.*, 85.

Then 1 gram of Cr. is combined with $\frac{85}{52} = 1.63$ grams $SO_4$.

$1.84 - 1.63 = 0.21$ gram $SO_4$ in the form of $H_2SO_4$ to be added for each gram of Cr.

$$\frac{\text{Grams Cr. in 100 cc.} \times 3785 \times 0.21 \times \frac{98}{96}}{453.6 \times 100} = x \text{ lb. } H_2SO_4 \text{ to be added per gallon.}$$

$$\frac{x}{\text{amt. of } H_2SO_4 \text{ in 1 lb. commercial } H_2SO_4 \text{ (0.935 lb.)}} = \text{lbs. commercial } H_2SO_4 \text{ to be added.}$$

*Summary.*

When there are less than 1.84 grams of $SO_4$ present for every gram of Cr., subtract this value from 1.84 and substitute the result in the equation given below:

$$\frac{\text{grams Cr. in 100 cc.} \times 38\ 607 \times ?}{424.1} \text{ or}$$

grams Cr. in 100 cc. $\times$ 0.091 $\times$ ? = pound commercial $H_2SO_4$ to be added per gallon of solution to give proper basicity.

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## THE BASICITY OF ONE-BATH CHROME SOLUTIONS.*

*By Frank N. Harrap, M.Sc., and Harry Hayes, B.Sc.*

The basicity of a one-bath liquor is expressed by the ratio $\frac{Cr}{SO_4}$ where for the sake of uniformity the Cr. is fixed as 52, the atomic weight of chromium. The salts $Cr_2(SO_4)_3$ and $Cr(OH)SO_4$ have, for example, respective basicities of $^{52}/_{144}$ $(= {}^{104}/_{288})$ and $^{52}/_{96}$. The solubility of a salt decreases as its basicity increases, and salts cannot be rendered basic (under ordinary conditions) beyond a certain solubility limit, approximately reached by a salt of the composition $Cr_3(OH)_5(SO_4)_2$ with a basicity of $^{52}/_{64}$ $(= {}^{156}/_{192})$.

Chromium is estimated by oxidizing the diluted chrome solution with $Na_2O_2$, and boiling to destroy excess of peroxide, when

* *Collegium*, London Edition, Nov., 1915, pp. 305-12.

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the chromium is converted into $Na_2CrO_4$. By the addition of concentrated HCl the excess of alkali is neutralized and the chromate converted into dichromate. This is estimated by titration with the thiosulphate solution after the addition of KI.

$$2Na_2CrO_4 + 4HCl = H_2Cr_2O_7 + H_2O + 4NaCl$$
$$H_2Cr_2O_7 + 6KI + 12HCl = 3I_2 + 2CrCl_3 + 6KCl + 7H_2O$$
$$3I_2 + 6Na_2S_2O_3 = 6NaI + 3Na_2S_4O_6$$
$$6Na_2S_2O_3 \equiv 3I_2 \equiv 2Na_2CrO_4 \equiv 2Cr.$$

$\therefore$ 1 cc. N/10 thiosulphate $\equiv$ 0.00173 gram Cr.

Sulphate (or chloride) is estimated by hydrolyzing the chrome salt and estimating the free acid thus produced.

$$e.g. \quad Cr(OH)SO_4 + 2H_2O \rightleftharpoons Cr(OH)_3 + H_2SO_4.$$

The rate of hydrolysis increases with rise of temperature and with increased dilution. The free acid is removed by various reagents, but all the methods are similar in principle, depending fundamentally upon a disturbance of this equilibrium between the basic chrome salt and its products of hydrolysis. Acid is removed from the solution, more basic salt hydrolyses, more acid is removed, and so on until hydrolysis is complete.

The six methods for the determination of the acid combined with chrome may be described briefly.

(1) Procter-McCandlish.—A given volume of solution is diluted to about 200 cc. and boiled in a porcelain basin. 3-4 cc. of 1 per cent. alcoholic phenolphthalein are added and the boiling solution titrated with N/2NaOH, stirring continuously. The end point is seen by the greyish tint of the liquid, or by a pink color on the sides of the basin, when the precipitate settles:

$$1 \text{ cc. N/2 NaOH} = 0.024 \text{ gram } (SO_4)$$

Stiasny uses baryta instead of sodium hydroxide.

(2) Körner.—The chrome solution is boiled with excess of standard NaOH. The mixture is poured into a graduated flask, filled to the mark when cool, shaken, and allowed to settle. A portion is pipetted off and titrated with standard HCl.

(3) Alden.—The diluted chrome solution is added slowly to a boiling solution of sodium carbonate, in excess. The mixture is boiled, cooled, and diluted to a known volume. After shaking and allowing to stand an aliquot portion is titrated with

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standard acid. The experiment is repeated with the amount of sodium carbonate used up in the first experiment and this second result is taken as correct.

(4) STIASNY.—To 10 cc. of chrome liquor (2-3 grams chrome oxide per liter) 10 cc. of 10 per cent. KI solution and about 0.5 gram $KIO_3$ are added 30 cc. N/10 thiosulphate solution are added and the mixture boiled for three to five minutes, and then cooled. Thiosulphate in excess is titrated with standard iodine and starch paste.

$$3H_2SO_4 + 5KI + KIO_3 = 3K_2SO_4 + 6I + 3H_2O$$

1 cc. N/10 iodine $\equiv$ 1 cc. N/10 thio-sulphate $\equiv$ 0.0048 gram ($SO_4$).

(5) BATESON.—The chrome solution is boiled with excess of ammonia, until phenolphthalein is reddened. The mixture is poured into a graduated flask, cooled, filled to the mark and shaken. After allowing to settle a definite volume is pipetted off. Excess of neutral (40 per cent.) formaldehyde is added and the solution titrated with standard NaOH to a very faint pink color.

N.B.—In Bateson's original paper the reference to boiling is omitted and the boiled solution is filtered.

*Theory.*—Chromium is precipitated as hydroxide and the acid yields an ammonium salt, which salt finally reacts with formaldehyde to regenerate free acid.

$$e.g.\ 2(NH_4)_2SO_4 + 6H.CHO = N(CH_2.N.CH_2)_3 + 2H_2SO_4 + 6H_2O$$

Excess of ammonia reacts with formaldehyde but gives no free acid.

$$4NH_3 + 6H.CHO = N(CH_2.N.CH_2)_3 + 6H_2O$$

(6) KOPECKY.—The chrome solution is boiled with magnesium carbonate for a long time, until $CO_2$ is given off. The liquid is cooled, filtered, and made up to a definite volume. Magnesium is estimated gravimetrically by the oxalate method. The authors suggest the replacement of $MgCO_3$ by $CuCO_3$, when it should be possible to determine any copper in the filtrate by the addition of acetic acid and KI and titration with thiosulphate and starch paste.

$$2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$$

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Of the six methods described, that of Kopecky is much too tedious, whilst those of Alden and Körner are practically identical. The basicity of a made up chrome liquor was determined by the authors, using the methods of Procter, Stiasny, Bateson and Körner.

(α) CHROMIUM.—This was roughly estimated in a preliminary experiment.

2 cc. original solution required 12.95 cc. N/10 thiosulphate.

∴ Cr. per liter = 12.95 × 0.00173 × 500 = 11.2 grams.

This result shows to what extent the original liquor must be diluted in order to get suitable burette readings.

| | Dilution | Vol. taken | N/10 thio required (mean) | Cr. per liter. Grams |
|---|---|---|---|---|
| Series A | 1 to 5 | 25 cc. | 31.95 cc. | 11.05 |
| Series B | 1 to 5 | 25 cc. | 31.9 cc. | 11.04 |

(β) SULPHATE.—In a preliminary experiment by the Procter method.

2 cc. original solution required 2.08 cc. N/2 NaOH

1 cc. N/10 NaOH = 0.024 gram ($SO_4$)

($SO_4$) per liter = 2 × 0.024 × 500 = 24 grams.

(1) PROCTER.

| | Vol. of original solution | Cc. N/2 NaOH (mean) | ($SO_4$) per liter. Grams |
|---|---|---|---|
| Series A | 25 cc. | 25.72 | 24.7 |
| Series B | 25 cc. | 25.6 | 24.6 |

Basicity is represented by $\frac{11.05}{24.65}$ $^{52}/_{116}$.

(2) STIASNY.

| Dilution | Vol. taken | Thio added | Iodine to titrate back (mean) | Thio used up | ($SO_4$) per liter grams | Basicity |
|---|---|---|---|---|---|---|
| 1 to 5 | 10 cc. | 30 cc. N/10 | 19.0 cc. N/10 | 11.0 cc. N/10 | 26.4 | $^{52}/_{124}$ |

(3) BATESON.

| | Dilution | Solution made up to Cc. | Volume titrated. Cc. | Vol. N/10 NaOH required. Cc. | ($SO_4$) per liter. Grams | Basicity |
|---|---|---|---|---|---|---|
| Series A (1) | 1 to 10 | 500 | 50 (filtered off) | 24.94 | 24 | $^{52}/_{113}$ |
| (2) | 1 to 10 | 500 | 50 (pipetted off) | 24.9 | 23.9 | $^{52}/_{112}$ |
| Series B | 1 to 10 | 500 | 50 (filtered) | 25.3 | 24.3 | $^{52}/_{114}$ |

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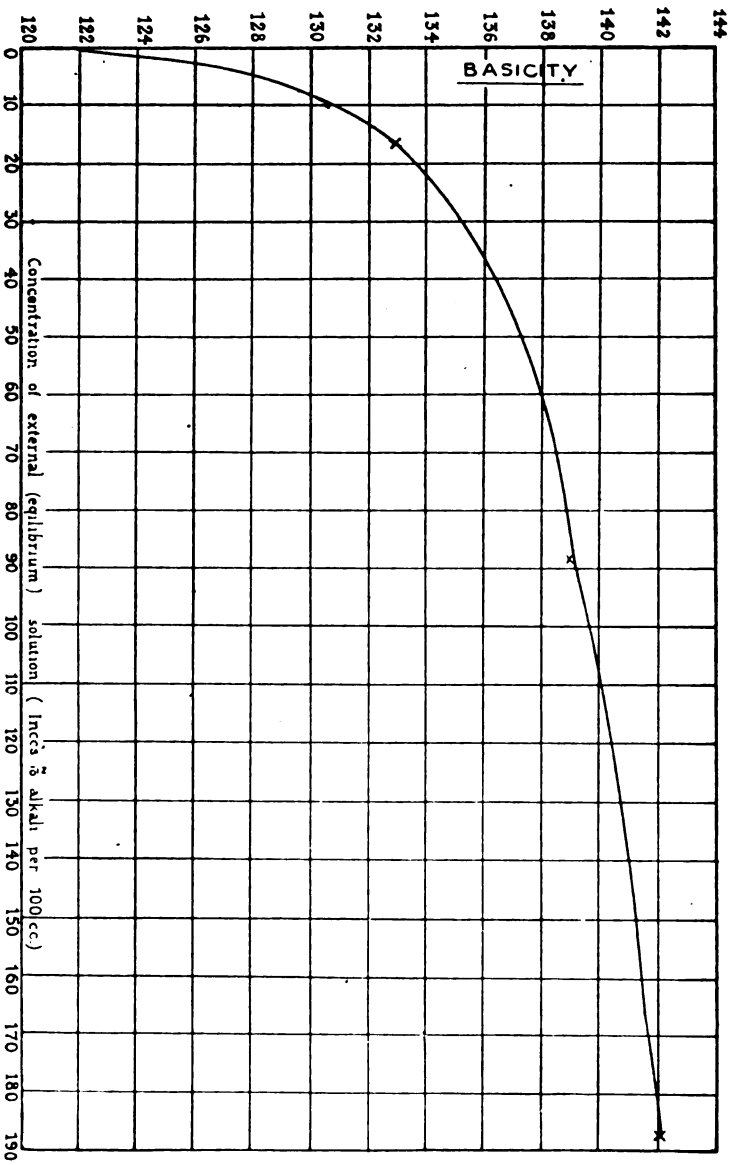


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(4) KÖRNER.

| | Dilution | Volume taken. Cc. | Alkali added. Cc. | Made up to Cc. | 100 cc. filtrate required. Cc. | Basicity |
|---|---|---|---|---|---|---|
| Series A (1) .... | 3 to 10 | 50 | 100 N/10 | 250 | 6.8 N/10 HCl | $^{52}/_{125}$ |
| (2) .... | original | 50 | 100 N/2 | 250 | 14.6 N/2 HCl | $^{52}/_{143}$ |
| Series B ..... | original | 50 | 100 " | 500 | 8.0 " " | $^{52}/_{136}$ |

It is evident that if sodium hydroxide is adsorbed by the precipitated chromium hydroxide, adsorption (and consequently the value found for the basicity), should be greatest when the concentration of the external alkali solution is at its maximum. The experiment was carried out of boiling 10 cc. of chrome solution with increasing amounts of alkali, pouring into 100 cc. flasks, and making up to the mark when cool. The flasks were well shaken, allowed to stand, and the filtered liquid titrated with acid.

| Cc. alkali added | Cc. alkali titrated back | Cc. alkali used up | Basicity |
|---|---|---|---|
| 15 cc. N/2 | 16.1 cc. N/10 | 58.9 cc. N/10 | 133 |
| 20 " " | 39.4 " " | 60.6 " " | 136.5 |
| 30 " " | 88.4 " " | 61.6 " " | 139 |
| 50 " " | 187.0 " " | 63.0 " " | 142 |

Plotting the value of the basicity against the concentration of the external solution when equilibrium is attained (which is given by column 2), a curve is obtained as in Fig. 1. It will be seen from the curve that the true basicity is about 122 and that the basicity found by experiment increases with increased concentration of alkali. The difficulty of volumetrically ascertaining the concentration of the external solution when very dilute renders the value 122 very uncertain, and it would be interesting to see results obtained by electrometric methods.

Now consider what results may be derived from a consideration of the adsorption formula

$$\frac{x}{m} = k\left(\frac{a-x}{v}\right)^{\frac{1}{p}}$$

where $a$ = total quantity of adsorbable material.
$x$ = quantity adsorbed.
$m$ = quantity of the adsorbent.
$v$ = volume of the solution.

Then $$\log \frac{x}{m} = \log k + \frac{1}{p} \log \left(\frac{a-x}{v}\right)$$

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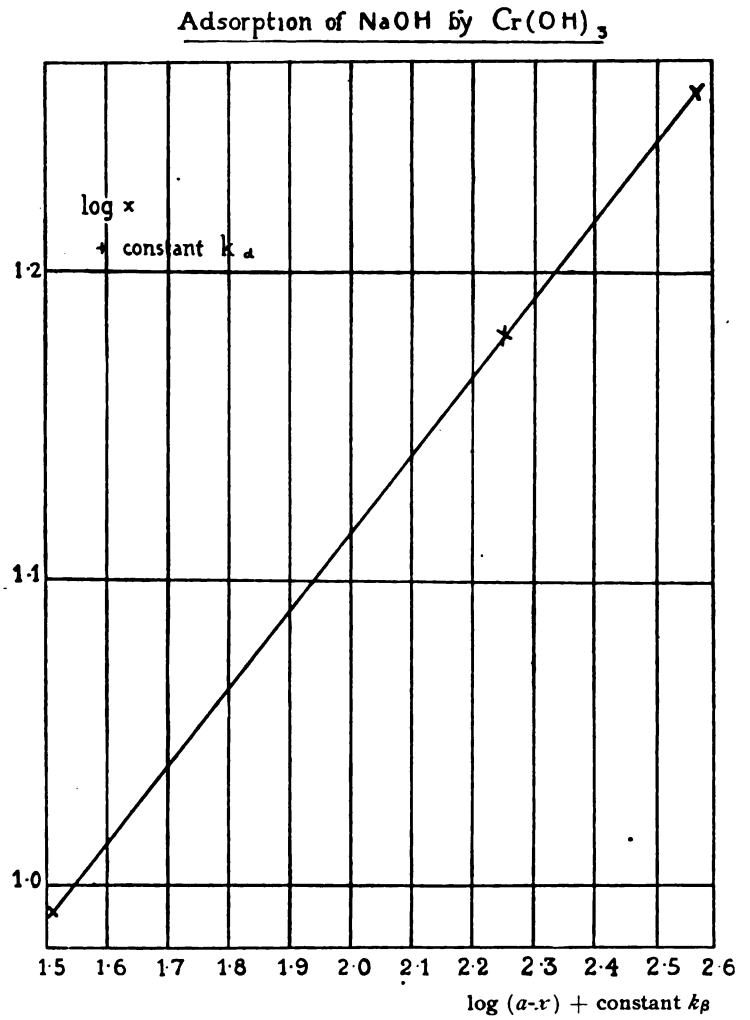


But in the case under examination $m$ and $v$ are constants.

$$\log x = \left(\log k + \log m - \frac{1}{p}\log v\right) + \frac{1}{p}\log (a\text{-}x)$$

$$\log x = C + \frac{1}{p}\log (a\text{-}x)$$

This equation is of the form $y = c + mx$, and therefore represents a straight line.

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If the true basicity be assumed to be 122 then $\frac{11.05}{a} = \frac{52}{122}$

where $a$ = grams $(SO_4)$ per liter = 25.9

Ten cc. of a solution of this strength would use up 10.8 cc. N/2 NaOH if no adsorption occurred.

The difference between 10.8 cc. and the amount of alkali actually used up gives a measure of the adsorption.

| Alkali added Cc. | Alkali titrated back | Alkali used up | Alkali adsorbed | Concentration of adsorbed alkali proportional to | Log of values in column 5 | Conc. of alkali in equilibrium solution proportional to | Log of values in column 7 |
|---|---|---|---|---|---|---|---|
| 15 N/2 | 3.22 N/2 | 11.78 N/2 | 0.98 N/2 | 9.8 | 0.99 | 32.2 | 1.51 |
| 20 " | 7.88 " | 12.12 " | 1.32 " | 13.2 | 1.12 | 78.8 | 1.90 |
| 30 " | 17.68 " | 12.32 " | 1.52 " | 15.2 | 1.18 | 176.8 | 2.25 |
| 50 " | 37.4 " | 12.6 " | 1.8 " | 18.0 | 1.26 | 374 | 2.57 |

When these logarithmic values are plotted they give a straight line as in Fig. 2.

## Criticism of the Various Methods.

1. Procter-McCandlish.—This is the most simple and rapid of the methods yet proposed, and probably the only one ever used in actual works' practice. It is easy to get good duplicates, and the end point is definite, although the pink color obtained is at first faint, possibly due to the high temperature and to adsorption of alkali as soon as excess is present. There is no alkali in excess until all the chrome is precipitated and, hence, no adsorption before the correct end point is reached. On the other hand, owing to the limited amount of alkali there is a tendency to the formation of a basic sulphate, instead of hydroxide, some of the $(SO_4)$ thus going into the precipitate and failing to neutralize its equivalent of alkali. One would expect Procter's method therefore to give results slightly lower than the actual basicity.

2. Stiasny.—Up to the liberation of iodine this is probably theoretically correct, but both KI and $KIO_3$, especially the latter, are liable to contain impurities which react with thiosulphate. Thiosulphate is also destroyed by decomposition on boiling, by adsorption, and by spurting. The results obtained for the basic-

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ity will thus be too high. It is probably best to add thiosulphate in very slight excess of the amount required, and to titrate back with iodine solution and starch paste, when the end point, even in the presence of the precipitate, is sharp to one drop. The loss of thiosulphate by boiling and spurting is then minimized.

3. BATESON.—Boiling is of course essential, and it is curious that in his original paper Bateson should omit any reference to boiling. It is better to pipette off the clear liquid rather than to filter, when the acidity or alkalinity of the filter paper and its adsorbent properties introduce complications. The adsorption of ammonia does not matter, but adsorption of ammonium salts tends to give too low results. Too low results are also obtained if any basic sulphate is precipitated. Old chrome liquors may contain amino acids, which give compounds with formaldehyde distinctly acid to phenolphthalein, and it must be remembered that the method is inapplicable to chrome liquors containing ammonium salts.

4. KÖRNER.—The results obtained by this method are not very encouraging. Alkali is carried down by the gelatinous precipitate of $Cr(OH)_3$, and the greater the amount of alkali in excess the greater the value found for the basicity. It would be interesting to see the results obtained by filtering off the precipitate from excess of alkali, washing the precipitate with hot water (to decompose any basic salt and to wash out adsorbed alkali), and finally titrating the mixed alkaline filtrates with a standard acid solution.

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## PETROLEUM LEATHER OILS.*

*By Charles R. Oberfell.*

### IMPORTANCE OF HYDROCARBON OILS.

On account of their merit the petroleum hydrocarbon oils have come into general use in recent years amongst manufacturers of all kinds of leather. Their importance as an adjunct to the industry is well established and if for no additional reason leather producers are much interested in any information about these oils as to their effect on the quality of the leather; but there is

* *Shoe and Leather Reporter*, Dec. 30, 1915.

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an additional reason which lies in the unsettled and rising market for petroleum products of all kinds. New quotations at increased prices are to be found in every tanner's mail these days so that the oil proposition is one of increasing importance.

Very little has been published for the guidance of the tanner in the purchasing or use of this product. There is ample information for all who wish to know concerning oils to be used for lubricating machinery, but an article by the writer in the JOURNAL of the American Leather Chemists Association in 1911 on the examination and valuation of petroleum hydrocarbon oils for leather use is the only contribution in recent years.

Since the publication of the above named paper, the writer has changed his opinion on certain points as the result of further study. This is particularly true of the value of certain laboratory tests, and the methods mentioned in this article have been found to be the only ones of practical value.

The commonly applied name to petroleum distillation products is "mineral" oils—this name in the strictest meaning is improper and misleading. "Mineral" applies more exactly to those oils which are extracted from natural shale formations and while their ultimate chemical composition may be similar to petroleum products it is the accepted opinion that their original formation was not from the same source. The term "mineral" also conveys the idea of inorganic origin while the petroleum products are thought to be the result of organic processes in nature.

The petroleum oils are also referred to as "hydrocarbon oils" which is quite true in a chemical sense, but it happens that there are hydrocarbon oils which come from widely divergent sources, as for illustration the oils resulting from the distillation of wool-grease under carefully controlled conditions. Aside from 5-10 per cent. of cholesterol, a substance belonging to the alcohol class, these distilled wool-grease oils are composed of hydrocarbon compounds which up to the present have defied differentiation by the chemist. Therefore to properly designate these hydrocarbon oils derived from crude petroleum it is necessary to refer to them as petroleum hydrocarbon oils.

## BLENDING PETROLEUM AND FISH OILS.

Petroleum hydrocarbon oils are always used for best results

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in conjunction with some other oil of fatty origin, usually of the whale oil group, or marine animal oils such as cod or menhaden oils. Cod oil is obtained from the liver of the cod fish, while menhaden oil comes from the blubber of the menhaden fish. These oils are drying oils, that is, they absorb oxygen from the air which converts them into a solid or semi-solid condition. This oxidized cod or menhaden oil has tanning properties which reaction is used to advantage in the manufacture of chamois leather. It probably acts as a tanning agent when contained in vegetable tanned leather, and thus we see that the marine animal oils in the fiber of leather probably change in time, and lose their full effect as a lubricant. In other words, they dry out. Petroleum hydrocarbon oils do not absorb oxygen, do not change in composition, and hence always exercise their lubricating function once impregnated in the fiber of the leather. For this reason they form a valuable adjunct to marine animal oils and will probably always be used. Even without the addition of a fatty oil the petroleum hydrocarbons will give a well lubricated, good feeling leather with no tendency to excessive greasiness, but it is advisable to use them blended as suggested above.

Petroleum hydrocarbons are found generally the world over, but here the supply comes from the United States and Mexico. They are usually divided into two classes based on the fact of whether they are obtained from paraffine base crude oil or asphaltic base crude. This is a chemical distinction, but the natural distinction shows in that the paraffine crudes are peculiar to Pennsylvania, Ohio and West Virginia or the northern crudes, while the asphaltic crudes include those produced in Texas, Oklahoma, California and Mexico, although the Mexican oils have the additional distinction of containing relatively high amounts of sulphur. This sulphur can be and is removed by refining methods designed for this purpose.

Whether derived from asphaltic or paraffine base crude petroleum the oil suitable for leather is obtained in essentially the same manner, but with different manufacturing details which gives one oil certain characteristics different from some other oil.

The general principles of the operations followed in refining crude oil should be understood if the leather producer is to have the information necessary to guard his best interests in purchas-

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ing, and a general outline of the refining processes is here given together with the products obtained.

As is commonly known oils are refined from crude petroleum by distillation methods. The usual form of still is similar to a horizontal steam boiler, its construction differing greatly, of course, but the comparison gives an idea of the form. The outlet from the still connects directly with the condenser, which is the cooling device for converting the vapors rising from the still into the liquid state. The fire is applied direct to the still and is regulated accordingly to the volatility of the product coming off; not so much heat is required for distilling gasoline and kerosene as for the heavier cylinder oil. The different grades of the product are selected by their gravity, samples being taken during distillation and as the gravity changes the products are run or "cut" as it is technically called, into separate receivers.

The first products distilling from a northern crude of Pennsylvania type is light ether or naphtha, then follow gasoline and kerosene or burning oil. After the kerosene but before the lubricating oils are distilled there is a product for which there is little direct use, it is now the aim, due to the value of gasoline, to convert this portion into gasoline. The process is known technically as "cracking" and has many variations.

After the burning oils obtained the distillation of the lubricating stock is assisted by direct superheated steam. This causes the oils to distill at lower temperatures and prevents scorching from the heated still walls. The hydrometer is the guide by which the various grades are separated. By testing the oils it is found that the fire test and viscosity rise as the gravity becomes heavier. It is at about this point that oils suitable for use on leather are produced, their varying quality being subject to the manipulation of the fire, steam, etc., in fact many conditions known to the practical refiner influence the quality of the products obtained.

After the oil of the desired characteristics is selected it is cleaned and bleached by treatment with sulphuric acid and caustic lye in a large cylindrical agitator, the agitation being accomplished with compressed air and the oil is heated by means of a steam coil. First the oil is agitated with the acid, the amount used depending on the condition of the stock and the final color

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desired. The waste or sludge obtained by this treatment is separated and the oil then receives the lye which neutralizes the excess acid. The caustic treatment also takes place in the agitator. After this the oil is washed with hot water until perfectly clean and neutral and is then run into settling tanks to separate all the water. In order to further improve the color the oil may be passed through a bone-charcoal or Fuller's earth filter. It may also be chilled and then pressed to influence the cold test and in some cases is subjected to the bleaching and mellowing action of the sun's rays and the atmosphere in shallow tanks set in the open.

In taking up the valuation of petroleum oils for their usefulness in leather manufacture it is necessary to consider each characteristic by itself and then draw a conclusion by a thorough weighing of all points including the selling price. All other conditions being equal, the oil which has the most desirable characteristics throughout would naturally be selected, but where characteristics of minor significance only are different and the price favors by one or several cents per gallon the oil with the least desirable minor characteristics it would be the best policy to select the cheapest oil.

The following characteristics should be taken into consideration for the valuation of petroleum hydrocarbon oils. Gravity, viscosity, emulsification, evaporation, acidity or alkalinity and to a lesser degree flash and fire point, and cold test are the characteristics which may be the basis for a chemist's report, but they do not compose a chemical analysis, because actually these are physical characteristics and when expressed numerically afford data for judging the physical fitness of the oil. A chemical analysis would involve what is termed an ultimate analysis or the determination of the percentage of carbon, hydrogen and oxygen which go to make up the oil molecules, obviously this chemical analysis would be of no value to a tanner.

The specific gravity of an oil means in simpler terms its weight compared with an equal volume of water and conveys its meaning best when expressed in pounds per cubic foot or per gallon, usually the latter. The gravity is measured most accurately by an instrument called the Westphal balance, but also, though less accurately, by a hydrometer. The gravity of oils is usually given

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in Baumé degrees. This is an arbitrary scale and for the connection between the degrees and specific gravity a table must be consulted. There are two Baumé scales, one for liquids heavier and one for liquids lighter than water, so that care must be used when consulting them. Peculiarly enough the lighter the Baumé degree of an oil the lower is its specific gravity; for illustration, a 30° oil is lighter than one of 23°. If the gravity is known the weight per gallon may be obtained by multiplying same by 8.33, the weight of a gallon of distilled water.

Oils suitable for leather range in weight from approximately 7¼ to 7¾ pounds per gallon, which on this maximum difference of ½ pound per gallon represents 2 tons on an 8,000-gallon tank car. In addition the gravity when considered along with other values aids the chemist in placing the geographical origin of the oil. There exists a certain connection between color and specific gravity, the lighter colored oils usually having a lighter gravity. However, the heavier gravity and darker colored oils can be filtered to a very light color.

Viscosity is the value of the internal (molecular) friction, but in lay terms means the "body" of the oil. It is quite apparent that either too thin or too thick an oil will not be suitable; if too thin it will drip off the leather and has little lubricating value, if too thick it will not penetrate the leather and follow the fibers to all parts, so that its value is lost either way. The viscosity may be measured by the Engler apparatus very suitably. Satisfactory Engler viscosimeters are now being manufactured in this country. An oil of proper body flows well when worked, sticks to the whole leather surface and eventually penetrates where it remains to lubricate. When referred to Engler degrees an oil having approximately 0.06 specific gravity for each degree viscosity has a satisfactory body. This figure is not to be accepted absolutely, but is to be used merely as a guide.

The emulsifying property seems to be of very great importance. It is influenced by the character of the stock and the mode of refining and finishing. Its importance lies in the fact of its activity in two capacities. Emulsification is the breaking up of the oil film with water into a mass of extremely small globules, so small that most of them cannot be seen with the eye; the smaller the globules the more perfect the emulsion.

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After leather has been oiled off and hung to dry to obtain a fair color the evaporation of the water must proceed from the flesh side, for if it evaporates from the "grain" the not yet solidified and uncombined tannin would be drawn to the surface by capillary force, there to be deposited and oxidized by the air, yielding a dark color and brittle surface. To force evaporation on the flesh a protective coating of oil is applied to the grain, which if it remains prevents the oxidation and when the leather has sufficiently dried it follows the path of the water along the fiber through to the flesh and remains deposited in the fibers. This protective coating of oil performs its work better if properly emulsified, otherwise it resists mixing with the water on the surface and eventually runs together in large oil sheets or films and not only exposes the surface to oxidation but drips onto the floor as well.

The more an oil is filtered the more it resists water or emulsification, conversely an oil which is exposed to the action of the sun's rays more readily forms an emulsion. Also petroleum oils may be made to emulsify by addition of many animal and vegetable fats as tallow or tallow oil, olive, neatsfoot, etc., but their presence affects the price and as a rule the tanner prefers to do his own blending. There is good judgment in this. No satisfactory tests have been devised for determining the emulsifying properties, although to one who is experienced this property can be readily recognized. The ease with which the oil forms emulsions, not the time required for the emulsion to break once it is formed, is the important fact. A simple unstandardized test, but one which gives much information, is to emulsify with the ball of a finger oil and a few drops of soft water in the palm of the hand.

It is a well known fact that some oils have greater lubricating properties than others, both on machinery and leather. This property is commonly referred to as "greasiness" and it is a physical characteristic for which no tests have been devised and which therefore cannot be expressed in simple figures. However, an oil can be robbed of greasiness for leather at the filter presses by too much chilling, so that the cold test may afford some information along this line, particularly so is this true of the oils refined from northern crudes.

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The difference in oils from northern and southern crudes is also brought out by the loss on heating, or the evaporation. Northern oils if properly refined should always show a loss of less than 1 per cent. when heated 15 hours at 212° F. while southern oils will normally show less than 5 per cent. It is only when these limits are exceeded that an oil may be considered unsuitable. The effect of too high volatile content is to produce a harsh feel and cut both in grain and fibers.

The oil should react neutral, that is, should not contain either acid or alkali remaining from the bleaches. Alkali is dangerous in that it makes dark tender leather, while sulphuric acid eventually causes deterioration.

The flash and fire point have no direct bearing on an oil's usefulness, that is, it cannot be said that an oil of high flash and fire test is more suitable for leather than one of lower values for these characteristics. These tests are of value to the tanner's chemist in connection with the cold test and gravity to determine the geographical origin of the oil.

As to the color of the oil it cannot be said that a pale oil will give a fairer leather than a darker or reddish oil, the color of the leather being more largely influenced by the emulsifying property.

There is too little common knowledge amongst users of leather oils about them for their own protection, and while it is impossible to lay down specifications for guidance now, the time is approaching when the tanner will no longer be dependent on the expert knowledge of the salesman.

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## ABSTRACTS.

**Use of Hypo in Tanning.** ANONYMOUS in *S. and L. Rep.*, Dec. 16 and 23, 1915. Hypo ($Na_2S_2O_3 8H_2O$) is used in the two-bath process of chrome tanning to reduce the bichromate of potash employed in the first bath. In this process, free sulphur is deposited on the fiber of the leather, thus giving to the two-bath leather some of its most characteristic properties. The rest of the article is essentially a repetition of the paper by Alfred Seymour-Jones, reprinted from *Collegium* in the January, 1913, number of the JOURNAL, pages 42 and following. Hide soaked in a solution of hypo is dehydrated, and the deposition of sulphur on the fiber effects a sort of tannage. One-bath chrome leather dipped in hypo solution is whitened by the deposit of sulphur. Hypo may also be used as a degreas-

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ing and as a depickling agent. It may also be used to lighten the color of vegetable tanning extracts.

**South African Tannins.** Vice-Consul EUGENE M. LAMB, Johannesburg, in *Commerce Reports.* The steady exhaustion of the world's supply of tanning materials, coupled with an increasing demand, lends new importance to the industry in those countries where it is capable of expansion. South Africa is one of these, for the wattle, sumac, "elandsboontjes," bastard sumac, and mangrove could all be produced here upon a commercial scale.

The bastard sumac, the least important of the varieties named, is found in the Transvaal, Orange River Colony, the highlands of Natal, and, though less frequently, in Southern and Northern Rhodesia. As the plant contains but a low percentage of tannin, it is doubtful whether it could profitably be exported.

"Elandsboontjes" (Elephantorrhiza burchellii, leguminosæ) is found in great abundance in the Transvaal, Orange River Colony, and in the uplands of Natal. The roots of "elandsboontjes" have been used for many years by the Boers for tanning, though it is said that the red color which this plant imparts to the leather, together with its tendency to render the leather unduly soft, reduces its value as a tanning material.

In his annual report for 1904-5 the Director of Agriculture, after describing certain experiments that had been carried on by his department, said:

"The following results indicate that the roots of Elephantorrhiza burchellii form a fairly satisfactory tanning material for local use, but that it is doubtful whether it would pay to export it. As a general rule it is not remunerative to export materials containing less than 30 per cent. of tannin unless, like sumac, they possess some particularly valuable characteristic not readily procurable in other tanning materials.

"It is possible that it might pay to prepare a tanning extract from the roots of Elephantorrhiza burchellii for export, but there are several difficulties in the way of doing this. The roots contain a considerable quantity of a reducing sugar which would find its way into the extract, and the latter would, therefore, be liable to ferment, and for that reason would be difficult to store or transport, especially in hot countries. Further, the red coloring matter present in the roots would also appear in the extract, and this would, to some extent, detract from its value as a tanning agent, especially in Europe. It would be possible to free the extract from this red coloring matter by bleaching it with sulphur dioxide or by the addition of sodium meta-bisulphite, but there is a certain amount of prejudice among tanners in European countries against the use of extract bleached in this way, and it is not advisable to adopt this plan if it can be avoided."

The production of wattle bark is an industry of much importance in South Africa. The bark is gathered from several species of acacia in Natal, Orange River Colony, and the Transvaal. Its most extensive use

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is in tanning heavy leathers, but it furnishes as well a full, soft finish with calfskin and can be used advantageously for the production of light leathers. Leather tanned with wattle bark has a faint reddish tinge, the color darkening slightly upon exposure to light, but not more so than that of leather tanned with oak or hemlock bark or extract.

Exports of tanning materials (wattle bark) from the Union of South Africa for the calendar year 1914 totaled $1,393,761, being the value of 130,216,826 pounds.

A matter of no little interest is the recent invention of a method of tannin extraction from wattle bark. The method heretofore employed involved the use of leaching vats. The new method comprises a primary crushing of the bark by a Krojenski crusher. Following this treatment the bark is passed through a series of heavy pressure bronze rollers. The important feature of this rolling is the moistening of the bark with warm water or with water and alcohol prior to its passage beneath the rolls.

Following a practical test of this method in the Johannesburg laboratories of the inventor, representative samples were taken of the green bark as used in the process and of the final liquor thus obtained. This liquid was found to have a specific gravity of 1.10 and was of a much better color than the liquids usually obtained by treating bark in leaching vats. It is claimed by the inventor that equally satisfactory results are obtained when dry or weathered bark is employed.

**Modern Methods of Blacking Chrome Leather.** ANONYMOUS in *S. and L. Rep.*, Jan., 1916. Logwood, used in conjunction with direct blacks, gives a leather with fuller "feel" than that dyed with direct blacks alone. Logwood for this purpose must not contain acid, the presence of which is recognized by a brown color, which changes to a violet red on addition of alkali. The skins are first drummed in hot water, then the neutralized logwood is added and then the direct black. For making a full leather, the addition of gambier with an acid black is satisfactory. Combination of logwood with titanium potassium oxalate gives a black which is uniform throughout the thickness of the leather.

**Canadians Use Sea-Lion Hides for Leather.** Consul O. GAYLORD MARSH, Ottawa, Canada, in *Commerce Reports*. On account of the growing demand for leather, by reason of war conditions, the hunting of sea lions and the use of sea-lion hides for leather are proposed as new industries for the Canadian Pacific coast. It is reported that a factory in British Columbia has made some excellent gloves, belting, and other leather articles from sea-lion hides.

**The Deliming Test.** ANONYMOUS in *S. and L. Rep.* In deliming limed goods by means of acids, it is usual to determine the completion of the process by applying to a freshly cut section of the pelt a solution of phenolphthalein. If such a solution is applied to limed pelt the section

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shows red, and if to a completely delimed pelt, there is no change of color. A partially delimed pelt will show red in the middle and colorless at the outsides. Most tanners usually allow the deliming to proceed to a given point. For some purposes complete deliming is necessary, whilst for others a mere surface deliming is sufficient. The amount of deliming necessary will depend on the nature of the subsequent process. For example, if it is a question of sheepskins which are first to be delimed with acid and then bated or puered, the first actual acid deliming is usually only carried out to such an extent that a streak of free lime is left in the middle. With heavier classes of goods, such as sole leather, the extent of the acid deliming will depend on the nature of the liquors into which the goods next proceed. If the end suspension liquors are very acid in character, it is not as important to neutralize as much lime as if these liquors were only slightly acid. The phenolphthalein test can be applied with almost any acid, but there is one caution which might be mentioned in its use, and that is that its action is more qualitative than quantitative. A trace of lime will give as strong a coloration with the phenolphthalein solution as a large quantity of free lime, and cases have been known in which this has led to confusion. To make the matter clear it may be well to take a definite example.

Suppose fully limed sole butts are being delimed with any of the ordinary acids and suppose that the amount of acid which is present in the liquor is not quite sufficient to neutralize the whole of the lime. At the commencement of the process the whole section will show red on application of phenolphthalein. After a short time the cut section will show red in the middle and colorless at the outsides. The depth of the outside strips will increase as the process goes on, until almost the whole of the acid has been neutralized by the free lime in the pelt. When this point has been reached, there will be a minimum red section in the center, but afterwards the free lime in the center will gradually diffuse out to the extremities, and so on application of phenolphthalein the whole section will show red. In this way it is quite possible for an almost completely delimed pelt to appear as though it were not at all delimed. It is in this sense that the test is qualitative rather than quantitative. By taking cut sections at different stages of the process and not only at the end, it is possible to determine more exactly the actual extent of the deliming.

**Glove Leather.** ANONYMOUS in *Hide and Leather*, Jan. 1, 1916. As kids change from milk to vegetable diet, their skins become firmer and less suitable for glove leather. This difference is not so marked in the case of sheep. The more wool and the better its quality the less suitable for glove leather is the skin. Dry skins are soaked in salt water to which sodium sulphide has been added, and drummed until soft. A mixture of sodium sulphide and lime in the proportion of 1 to 4 is slaked and made into a paste which is painted onto the flesh side. After 12 hours the wool or hair can be scraped off. The skins are now limed from 7 to 14

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days and then fleshed. Deliming is done in a paddle, at a temperature of 90° F., formic acid and salt being added a little at a time until the phenolphthalein test shows no color. The next treatment is puering, after which the skins are worked out on the grain side. A mixture of 2 parts bran and 1 part flour is scalded to make the drench, in which the goods lie over night at 95° F. Tanning or "dressing" may be done with alum, salt and flour, or with sulphate of alumina. In the latter case, the skins are first pickled with sulphuric acid and salt: for 100 pounds of skins, 1¼ pounds of acid and 17 pounds of salt are added to 16 gallons of water, and the goods drummed in this for 2 hours. To prepare the tanning liquor, dissolve 14 pounds of sulphate of alumina in 10 gallons of water and 1¾ pounds of bicarbonate of soda in 1 gallon of water. Add the latter solution to the former, slowly and with constant stirring. Drum the skins for 20 minutes with 11 gallons of water to which 3 pounds of salt and 1¼ pounds of Glauber salt have been added, then draw off the solution and drum for 20 minutes with a fresh solution of 5 pounds of salt in 11 gallons of water. Then pour in one-half of the alumina and soda and run 3 hours. Now take out the skins and horse up over night. Then hang up to dry. Put back in drum with 9 gallons of water and run 10 minutes, when the rest of the alum and soda is added, and the drum run 3 hours more. Dry and let them remain dry for 2 weeks. Before dyeing the skins must be treated with a warm solution of soda ash.

**Fermentation of Tan Liquors.** DR. HUGO KUHL, *Ledertechnische Rundschau,* Sept. 2, 1915. Alcoholic fermentation soon sets in in fresh infusions of vegetable tanning materials. The intensity of this fermentation depends on the kind of material and the sugar content of the liquor. The alcohol is afterward further fermented to acetic acid by the action of bacteria and yeasts. If the liquor is at rest, a film, "mycoderm," tends to form on the surface, which influences unfavorably the normal fermentation. The formation of this film can often be prevented by keeping the liquors agitated. A third fermentation, producing lactic acid, may be caused in various ways. Andreasch distinguished four kinds of organisms which produced lactic acid. In old liquors, the so-called "permanent coloring liquors," which are strengthened by filling up with fresher liquors, a butyric fermentation often takes place, which results in the production of a less firm leather than is desirable. The saving of cost by using these old liquors is therefore only apparent, and the old liquors had better be thrown away and only relatively fresh ones, which are easily controlled, used. If after the sweating process, hides are insufficiently washed, bacteria of decay are brought into the weak liquors, where they may do serious damage to the hide by continuing to grow and cause further decay of hide substance. If the early liquors are sufficiently acid, these bacteria cannot grow. A patent issued in 1909 proposes to tan hides with completely fermented materials, claiming that by using such liquors in a drum, a saving of 60 per cent. of tannin over the ordinary process may be made. The inventor proposes to ferment the bark or tan-wood

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by piling it in a closed room and wetting it with a ferment liquor made of 10 parts water to 1 part whey. Brighter color for the resulting leather is said to be one effect of this process. Since whey is rich in lactic bacteria, the cause of the fermentation of the tanning material is evident. The author carried out a research in this direction with pure cultures of several lactic acid forming organisms. A mixture was made of 4 parts whey to 1 of water, and sterilized on three successive days. This mixture was then inoculated with a pure culture of one of the organisms, and after it had been kept for some time in an incubator so as to be rich in the organism which had been planted in it, the tanning material was wetted with it. The extraction of the material was carried out in a manner which excluded contamination from the air, at a temperature most favorable for the growth of lactic bacteria, that is from 38° to 42° C. (99° to 107° F.). At first an active alcoholic fermentation took place, then lactic fermentation. By means of a parallel experiment, it was shown that the yield of extract is notably increased by extracting the material with a culture of lactic acid organisms instead of water. In the fresh liquor, rich in tannin, the formation of lactic acid is limited by the tannin, which hinders the growth of the lactic acid forming organisms, and permits the more resistant yeasts and moulds to grow. Even if the progress of the fermentation is successfully regulated, there is always the danger of infection from the water used, from the air or from the hide itself. The more carefully the work is done, the less the danger of contaminating the liquors, and so the more likely is the tannage to be successful. If one wishes to work with liquors in which acids are produced by fermentation, he will do well to use definite cultures of lactic organisms, rather than a mixture of water and whey, which is liable to contain the germs of various unfriendly fermentations. It is worth while to use for extraction water which has been sterilized by heat, and if the hides have been sweated, to rinse them very thoroughly before they are put in the liquors. L. B.

**The Levi-Orthmann Method of Tannin Estimation.** R. LAUFFMANN. *Ledertechnische Rundschau,* Sept. 23, 1915. The method in question involves the use of "reagent 33," first described by Levi and Orthmann in this JOURNAL, Vol. 6, p. 474. Further details of method and results are given in three articles in Vol. 8, pp. 40-42, 161-4 and 308-12. The latest published description of the method is in the July, 1915, JOURNAL, p. 360. Lauffmann reviews the published material, remarking that Levi and Orthmann's tannin factor, based on the hypothetical monoglucoside $C_{20}H_{30}O_{14}$ cannot be correct for all tannins unless they all have the same molecular constitution, which is known not to be the case. A different factor would therefore have to be used for each tannin if the results are to be comparable to those obtained by the hide powder method, as is the case with the Löwenthal method, which makes use of the reducing power of tannin upon $KMnO_4$ in the presence of indigotin. It seems also that the difficulty is greater in the case of reagent 33, since even tanning materials of the

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same kind give results which vary widely. There is also another cause of error in the Levi-Orthmann method, because not only tannin, but also non-tannins absorb iodine in small quantities, and sulphite-cellulose extract absorbs notable quantities. This results in the titration with thiosulphate giving too low results, and so gives too high figures for tannin. The following table gives the author's results in a number of cases, comparing the Levi-Orthmann method with the hide powder shake method. Columns headed *a* and *b* are separate determinations, column *m* being mean results, all figures being percentages.

TABLE OF COMPARATIVE RESULTS BY THE TWO METHODS.

| | Levi-Orthmann | | | Shake method | | |
|---|---|---|---|---|---|---|
| | *a* | *b* | *m* | *a* | *b* | *m* |
| **Tanning Materials.** | | | | | | |
| Oak bark | 13.3 | 13.0 | 13.1 | 13.6 | 13.4 | 13.5 |
| Oak bark | 12.5 | 12.0 | 12.2 | 11.2 | 10.9 | 11.0 |
| Fir bark ("Fichten") | 10.0 | 10.1 | 10.0 | 11.8 | 11.9 | 11.8 |
| Fir bark | 7.0 | 7.2 | 7.1 | 10.1 | 10.2 | 10.1 |
| Fir bark | 8.4 | 8.0 | 8.2 | 11.7 | 11.6 | 11.6 |
| Mangrove bark | 36.8 | 35.2 | 36.0 | 31.9 | 31.8 | 32.4* |
| Mangrove bark | 34.3 | 33.2 | 33.8 | 29.2 | 29.4 | 29.3 |
| Mimosa bark | 35.5 | 35.9 | 35.7 | 34.2 | 34.6 | 34.4 |
| Trillo | 33.4 | 32.3 | 32.9 | 34.2 | 34.4 | 34.3 |
| Knoppern | 40.1 | 40.3 | 40.2 | 34.8 | 35.2 | 35.0 |
| **Tannin and Cellulose Extracts.** | | | | | | |
| Quebracho | 29.4 | 30.3 | 29.9 | 29.7 | 28.8 | 29.3 |
| Quebracho | 32.3 | 31.1 | 31.7 | 29.2 | 28.8 | 29.0 |
| Chestnut wood | 25.9 | 26.0 | 25.9 | 24.7 | 23.7 | 24.2 |
| Chestnut wood | 35.5 | 35.9 | 35.7 | 33.3 | 33.6 | 33.4 |
| Oak wood | 25.4 | 25.3 | 25.3 | 24.1 | 24.3 | 24.2 |
| Oak wood | 20.1 | 20.2 | 20.1 | 20.6 | 20.4 | 20.5 |
| Oak bark | 18.0 | 18.1 | 18.0 | 19.3 | 19.0 | 19.1 |
| Myrobalans | 17.1 | 15.4 | 16.3 | 21.0 | 20.6 | 20.8 |
| Mimosa bark | 29.8 | 29.9 | 29.8 | 25.8 | 25.6 | 25.7 |
| Cellulose | 6.5 | -- | — | 18.7 | — | — |
| Cellulose | 5.2 | 5.0 | 5.1 | 15.7 | 16.3 | 16.0 |

* There is evidently a typographical error here in the original, and there are no means of judging which number is wrong.

The author's results by the new method, as well as the published results of Levi and Orthmann, differ from those by the hide powder method; in some instances slightly, but in the majority of instances more or less widely. Materials of the same kind give higher results by one method in one case and by the other method in another. The very low results by the new method in the case of cellulose extract are consistent with those obtained by the authors of the method, they having found 5 per cent. in one cellulose extract and none in another. On this

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behavior of cellulose extract by the new method the authors have sought to base a process for the recognition of cellulose extract and its estimation in mixture with tanning extracts, determining the tannin content both by the new method and by the shake method with hide powder, and estimating the amount of cellulose extract from the difference between these results. On account of the considerable variations in the "tannin" content of cellulose extract as shown by the new method, figures obtained in the manner described would seem to be liable to rather grave uncertainty. The author remarks that in the case of the cellulose extracts which he examined, not the slightest precipitate was observable on addition of the chromium compound (reagent 33), and he attributes the apparent "tannin" result to the absorption of iodine by materials present in the extract. The error caused by the absorption of iodine in titrating the chromium with thiosulphate solution is greater in the case of the cellulose extract than in that of a tannin extract because in the latter case most of the iodine absorbing material has been precipitated out by the chromium compound before the iodine is added, while in the former all the material is present in the solution along with the iodine at the time of titration. The above results indicate that the Levi-Orthmann method presents no advantages over the hide-powder process, but there is no apparent reason why it cannot, like the Löwenthal method, be used to advantage in tannery control, where the same materials are being used month after month. L. B.

**Some Points on Water Softening.** F. A. ANDERSON, *J. S. C. I.*, Dec. 15, 1915, pp.1180-2. The four factors which must in general be known are free $CO_2$, alkalinity, or carbonate hardness, total lime and total magnesia. Free $CO_2$ is generally so small in amount as to be negligible. Seyler's method for estimating it is to titrate with a dilute standard $Na_2CO_3$, using phenolphthalein, until a slight permanent pink develops. Alkalinity is found by titrating in the cold with HCl, and methyl orange. Total lime and magnesia may be found by the ordinary methods, but these are laborious. The soap test is of little value. The Lunge-Pfeifer method allows both lime and magnesia to be estimated with tolerable accuracy. It is as follows: 100 cc. of the water is made acid with HCl, concentrated to 30 cc., washed into a 100 cc. flask, a drop of methyl orange added and the liquid neutralized. Ten cc. each of N/10 NaOH and $Na_2CO_3$ are added, and the whole boiled 2 or 3 minutes, precipitating the Ca and Mg completely as carbonate and hydroxide respectively. Cool, make up to the mark and filter through a dry filter. Titrate 50 cc. of filtrate with N/10 acid, to determine excess alkali. The amount of lime and magnesia is found from the loss of alkalinity observed. Magnesia alone may be found by using NaOH only, in the cold, in a stoppered cylinder instead of a flask, and after allowing the liquid to settle clear, titrating an aliquot part of the supernatant liquid. Exclusion of $CO_2$ is thus accomplished, and the Mg alone may be found.

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## PROPOSED ADDITIONS TO METHODS.

### ANALYSIS OF ONE-BATH CHROME LIQUORS.

*Chrome Determination.*—Dilute a measured quantity of the liquor with water to a definite volume so that the dilution contains from 0.15 to 0.25 per cent. of $Cr_2O_3$. To 10 cc. of this dilution in a 300 cc. Erlenmeyer flask add about 50 cc. of water and about 2 grams of sodium peroxide. Boil gently 30 minutes, adding water if necessary to keep the volume from falling below about 15 cc. Cool, neutralize with strong HCl and add 5 cc. excess. Cool again. Add 10 cc. of a 10 per cent. solution of potassium iodide. After 1 minute run in from a burette 0.1 N sodium thio-

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sulphate until the iodine color has nearly disappeared; then add a few cc. of starch solution (1 gram per liter) and titrate to the disappearance of the blue. One cc. of 0.1 N thiosulphate is equivalent to 0.002533 gram $Cr_2O_3$.

*Acid Determination.*—Place 50 cc. of the above dilution in a 7-inch porcelain dish, add about 400 cc. of water and 1 cc. of a 5 per cent. solution of phenolphthalein and bring to a boil. While boiling, titrate with 0.5 N NaOH until the pink color persists after 1 minute boiling. One cc. 0.5 N NaOH is equivalent to 0.02002 gram $SO_3$, 0.02452 gram $H_2SO_4$, 0.01773 gram Cl or 0.01823 gram HCl.

*Basicity.*—The basicity is the ratio of basic radical to acid radical, found by dividing the percentage of $Cr_2O_3$ by the percentage of $SO_3$ or of Cl, carrying the quotient to two decimal places.

### Analysis of Chrome Leather.

*Chrome Determination.*—(*a*) Ash 3 grams of leather. Mix the ash well with 4 grams of a mixture of equal parts of sodium carbonate, potassium carbonate and powdered borax glass and fuse for 30 minutes. Dissolve the cooled fusion in hot water with enough HCl to make the solution acid. Filter. If there is any residue on the filter, ash it and treat the ash with 1 gram of the fushion mixture in the same manner as the original ash, adding the solution to the first. Make up to 500 cc. To 100 cc. of this solution in an Erlenmeyer flask, add 5 cc. HCl and proceed as above.

(*b*) If it is not desired to determine Fe or Al, the ash of 3 grams of leather may be transferred to an iron crucible, mixed with 3 grams of sodium peroxide and fused 10 minutes. Place cooled crucible in 300 cc. water in a casserole and boil 20 minutes. Wash into a 500 cc. flask, cool and make up to the mark. Filter through a dry filter. Place 100 cc. of filtrate in Erlenmeyer, neutralize with HCl, add 5 cc. excess and proceed as above.

### Analysis of Lactic Acid.

*Free Sulphuric Acid.*—Dissolve 50 grams of the sample in 200 cc. alcohol, which should be neutral, and of at least 95 per cent. strength. Heat to 60° C., cover and let stand overnight in a warm place. Filter off precipitated material and wash with al-

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cohol. Evaporate off the alcohol, make up residue to 250 cc. with water, add 5 cc. strong HCl, boil, add $BaCl_2$ and determine $BaSO_4$ in the usual way. Calculate to per cent. $H_2SO_4$ on the original sample.

*Volatile Acid.*—Weigh out 1 gram of sample, make up to about 50 cc. with water, titrate with 0.5 N NaOH. Calculate the result to lactic acid: (1 cc. 0.5 N NaOH = 0.045 gram lactic acid.) On this basis, make up a solution containing about 15 grams of acid per liter. Place 150 cc. of this dilution in a long-necked 300 cc. Kjeldahl flask, connected through a Kjeldhal bulb trap to a vertical spiral condenser, the total height from the bottom of the flask to the top of the turn connecting with the condenser being between 20 and 24 inches. Distill over 125 cc. in from 47 to 53 minutes, counting from the time the first drop falls into the receiver, which should be a graduated cylinder. Add 125 cc. of water to the residue in the flask and repeat. Titrate both distillates with 0.1 N NaOH and phenolphthalein and calculate result to grams of acetic acid: 1 cc. 0.1 N NaOH = 0.006 gram acetic acid. From these figures for acid found in distillates find actual weight of volatile acid placed in boiling flask, by means of table, (see p. 96), and calculate this result to percentage of volatile acid in the sample.

*Free Acid and Anhydride.*—Titrate 50 cc. of the dilution made up for volatile acid, in the cold, with 0.5 N NaOH and phenolphthalein to first full pink. Call this figure "first titration." From it subtract a number of cc. of 0.5 N NaOH equivalent to the sum of volatile acid and free sulphuric acid present in the 50 cc. of dilution. (If the sample contains free oxalic or hydrochloric acid, the amount must be determined by appropriate methods, and further deduction made.) Calculate the remainder to lactic acid and express it as a percentage of the sample. This is the free lactic acid. After completing the first titration, add 4 cc. excess alkali, or in the case of concentrated acids 5 cc., and stand aside at room temperature (20-25° C.), for 15 minutes. Then add 5 cc. 0.5 N $H_2SO_4$, boil, and titrate back with 0.5 N NaOH. The amount of alkali used by anhydride is now found by subtraction and calculated to lactic acid. Express this as per cent. of lactic acid equivalent to anhydride present in sample.

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## REPORT OF COMMITTEE FOR MELTING POINT OF GREASES (OTHER THAN PARAFFINE WAX.)

T. A. FAUST, *Chairman.*

The results of the work carried out by last year's Committee showed such poor concordance, that the method as outlined at that time was deemed unsatisfactory. The Committee was therefore re-appointed to give this matter further consideration.

Last year's work rather indicated that the thermometer bulb method was the most promising, although it was suggested that the Ubbelohde thermometer be given a thorough trial.

The Ubbelohde thermometer is in reality a standardized thermometer bulb apparatus, the readings being taken at the protruding point and at the drop point; the former being the temperature at which the grease begins to slip on the bulb, and the latter the temperature at which a clear drop protrudes through a small orifice directly below the bottom of the bulb. It would seem, therefore, that the drop point should agree with the melting point as found by the thermometer bulb method, but from the observations of the writer, this does not appear to be the case.

The advocates of the Ubbelohde thermometer method have insisted that it is the only dependable one, and the Chairman attempted to secure several of these instruments for the Committee work. However, it developed that no instruments were available, and attempts to have these instruments made to order by various concerns in this country were not successful.

The Chairman therefore made a few changes in the thermometer bulb method as used last year, and submitted it to the Committee for their criticisms, and then re-wrote the entire method according to the suggestions and sentiment of the collaborators, and again submitted it to the Committee, together with two samples of grease for collaborative work.

This method, together with the results obtained by the Committee, follows:

### *Suggested Method for Melting Point of Greases (other than Paraffine Wax) Thermometer Bulb Method.*

Dip a thermometer having a bulb not less than 5/8 inch nor more than 3/4 inch long, into the melted grease to the depth of

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the bulb, the grease being at a temperature approximately 10° above its melting point. Allow the thermometer to remain in the grease 5 seconds, remove, rotate slowly in a vertical position, and before quite solidified, remove excess drop of grease on bottom of bulb by touching to the hand.

After standing over night, place the thermometer in a test tube 6 inches x 1 inch, and cork lightly so that the bulb is 1 inch from the bottom of the tube. Suspend the test tube and thermometer in a beaker of water, the bottom of the test tube being about 1 inch above the bottom of the beaker. Place a flame underneath, and gradually raise the temperature of the water to about 15° below the probable melting point, and then raise the temperature not less than 1° nor more than 1½° per minute, until a drop of clear grease forms on the bottom of the bulb. This temperature represents the melting point.

Results obtained by the Committee:

| | A | B |
|---|---|---|
| Alsop & Cuthbert | 51.2° C. | 47.4° C. |
| Eachus | 50° | 48° |
| Kernahan | 52° | 48° |
| Oberfell | 53° | 48° |
| Orthmann | 52° | 48.2° |
| Small & Vaudreuil | 53.4° | 49.2° |
| Sprague | 52° | 48° |
| Faust | 51.1° | 48.3° |

The remarks of the collaborators are as follows:

ALSOP: The specified length of the test tube is rather inconvenient for the average thermometer, in that the cork has to be cut away in order to make the reading.

EACHUS: Neither sample would melt clear before dipping the thermometer into the melted grease, probably due to the fact that the samples evidently contained dirt and moisture, and this fact makes the determinations less accurate.

OBERFELL: I believe the method takes care of all the conditions, excepting possibly the inaccuracies of the ordinary chemical thermometers, in that they are far from accurate when supplied by the makers, and in addition, undergo changes due to age, molecular re-arrangements, and continual contraction and expansion while in use. Also, note must be taken of the fact that various thermometers are scaled for various immersions, which

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will make a difference. Cooled boiled water is suggested in order to eliminate air bubbles. I do not believe that the Ubbelohde method will show any advantage over this suggested method.

ORTHMANN: I am still of the same opinion as last year, that the Ubbelohde melting point method is superior, and I trust that we will soon be able to take up this method.

SMALL & VAUDREUIL: Believe that the rapidity with which the temperature of the water is raised as the melting point is approached, is too great, and would suggest the following change in the last two sentences: "Place a flame underneath, and gradually raise the temperature of the water to about 5° below the probable melting point. The temperature is then to be raised at a rate not exceeding 1° in 2 minutes until a drop of clear grease forms on the bottom of the bulb. This temperature represents the melting point."

SPRAGUE: It was not specified whether the Fahrenheit or Centigrade thermometer was to be used, but suggest the Centigrade.

SUMMARY: The results as shown in the table indicate good concordance, especially in view of the fact that poor grade greases were selected, so as to give the method as severe a test as possible; the surprising feature, however, being that sample B which was a very poor grade mixed grease, showed better concordance than sample A, which was a fair quality of stearine. On sample A, none of the results differed much over 1° from the average, and on sample B, they were even closer.

Attention should be given to the remarks of Small & Vaudreuil, regarding the rapidity of raising the temperature when the melting point is approached, but the Chairman thought the results indicated sufficient concordance, and thought that no further alteration of the method was necessary.

The general sentiment of the Committee was in favor of the above method rather than the Ubbelohde thermometer, but it may develop that this method will have to be tested at a later date.

It is understood that the Centigrade thermometer shall be used.

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## REPORT OF COMMITTEE ON MISCELLANEOUS METHODS.

*By Lloyd Balderston, Chairman.*

The only collaborative work done by this committee since the 1915 meeting has been the preparation of a table for estimation of volatile acid in lactic acid. Of the many members asked, three promised to do the work, but the only one who found it possible to send in results was Mr. W. C. Carnell. A sample of C. P. concentrated lactic acid was sent out, with directions for making up solutions containing approximately 1.5 per cent. total acid, and having the following percentages of acetic acid, reckoned on the amounts of sample plus added acetic acid: 0, 0.5, 1, 1.5, 2, 2.5, 3. At least four distillations were to be made of each of these seven dilutions, the manner of distillation being the same as that described in the previous report, and repeated in the proposed method of this issue, p. 91.

TABLE SHOWING RESULTS OF DISTILLATION TESTS ON MIXTURES OF LACTIC AND ACETIC ACIDS.

Figures in third and fourth column are means of four distillation tests.

| The dilutions distilled were made up to correspond to percentages of volatile acid in the original sample, as below | g. acetic acid in the 150 cc. put into boiling flask | Observer | g. acetic acid found in first distillate | g. acetic acid found in both distillates |
|---|---|---|---|---|
| 0 | 0 | W.C.C. | 0.0025 | 0.0047 |
| | | L. B. | 0.0033 | 0.0063 |
| 0.5 | 0.0128 | W.C.C. | 0.0107 | 0.0155 |
| | | L. B. | 00.116 | 0.0181 |
| 1.0 | 0.0256 | W.C.C. | 0.0190 | 0.0273 |
| | | L. B. | 0.0195 | 0.0282 |
| 1.5 | 0.0386 | W.C.C. | 0.0266 | 0.0387 |
| | | L. B. | 0.0291 | 0.0421 |
| 2.0 | 0.0518 | W.C.C. | 0.0347 | 0.0478 |
| | | L. B. | 0.0367 | 0.0520 |
| 2.5 | 0.0651 | W.C.C. | 0.0432 | 0.0598 |
| | | L. B. | 0.0444 | 0.0628 |
| 3.0 | 0.0785 | W.C.C. | 0.0512 | 0.0709 |
| | | L. B. | 0.0519 | 0.0730 |

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TABLE SHOWING THE RELATION OF AMOUNTS OF VOLATILE ACID FOUND IN DISTILLATE OBTAINED UNDER STANDARD CONDITIONS TO THE AMOUNTS ACTUALLY PRESENT IN DISTILLING FLASK, IN MG.

One Distillation.

| In distillate | In flask | In distillate | In flask |
|---|---|---|---|
| 1 | 0 | 26 | 35.9 |
| 2 | 0 | 27 | 37.5 |
| 3 | 0 | 28 | 39.0 |
| 4 | 2.0 | 29 | 40.6 |
| 5 | 3.5 | 30 | 42.1 |
| 6 | 5.1 | 31 | 43.7 |
| 7 | 6.7 | 32 | 45.2 |
| 8 | 8.2 | 33 | 46.8 |
| 9 | 9.8 | 34 | 48.3 |
| 10 | 11.3 | 35 | 49.9 |
| 11 | 12.8 | 36 | 51.5 |
| 12 | 14.4 | 37 | 53.1 |
| 13 | 15.9 | 38 | 54.7 |
| 14 | 17.5 | 39 | 56.3 |
| 15 | 19.0 | 40 | 57.9 |
| 16 | 20.5 | 41 | 59.6 |
| 17 | 22.1 | 42 | 61.3 |
| 18 | 23.6 | 43 | 62.9 |
| 19 | 25.2 | 44 | 64.6 |
| 20 | 26.7 | 45 | 66.3 |
| 21 | 28.2 | 46 | 68.0 |
| 22 | 29.8 | 47 | 69.8 |
| 23 | 31.3 | 48 | 71.5 |
| 24 | 32.9 | 49 | 73.3 |
| 25 | 34.4 | 50 | 75.0 |

Two Distillations.

| In distillates | In flask | In distillates | In flask |
|---|---|---|---|
| 5 | 0 | 38 | 37.7 |
| 6 | 1.0 | 39 | 38.9 |
| 7 | 2.0 | 40 | 40.0 |
| 8 | 3.0 | 41 | 41.1 |
| 9 | 4.0 | 42 | 42.3 |
| 10 | 5.0 | 43 | 43.4 |
| 11 | 6.2 | 44 | 44.6 |
| 12 | 7.4 | 45 | 45.7 |
| 13 | 8.6 | 46 | 46.8 |
| 14 | 9.8 | 47 | 48.0 |
| 15 | 11.0 | 48 | 49.2 |
| 16 | 12.1 | 49 | 50.3 |
| 17 | 13.4 | 50 | 51.5 |
| 18 | 14.5 | 51 | 52.7 |
| 19 | 15.7 | 52 | 53.9 |

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| In distillates | In flask | In distillates | In flask |
|---|---|---|---|
| 20 | 16.9 | 53 | 55.0 |
| 21 | 18.1 | 54 | 56.2 |
| 22 | 19.2 | 55 | 57.4 |
| 23 | 20.4 | 56 | 58.6 |
| 24 | 21.5 | 57 | 59.8 |
| 25 | 22.7 | 58 | 61.1 |
| 26 | 23.9 | 59 | 62.3 |
| 27 | 25.0 | 60 | 63.5 |
| 28 | 26.2 | 61 | 64.7 |
| 29 | 27.3 | 62 | 65.9 |
| 30 | 28.5 | 63 | 67.2 |
| 31 | 29.7 | 64 | 68.4 |
| 32 | 30.8 | 65 | 69.6 |
| 33 | 32.0 | 66 | 70.8 |
| 34 | 33.1 | 67 | 72.0 |
| 35 | 34.3 | 68 | 73.3 |
| 36 | 35.4 | 69 | 74.5 |
| 37 | 36.6 | 70 | 75.7 |

Results are given in the table on page 95. From averages of these results curves were plotted showing the relation of amount of acid found by titration in one distillate and in both distillates to the actual amount of volatile acid present in the distilling flask. From these curves, the table (pages 96-97) was constructed. It will be recalled that whenever a dilution of lactic acid is distilled some of the lactic acid is carried over, which accounts for the fact that when the amount of volatile acid is very small the table shows less than the titrations would seem to indicate.

The chairman is sorry to turn in a table based on so few independent sets of results, but believes it will be found to be very nearly correct.

Proposed methods for analysis of chrome leather and chrome liquors are published in the present issue, as well as those for lactic acid. Practice in regard to calculation of basicity of one-bath chrome liquors is quite diverse, but the weight of opinion seems to favor the method given in the proposed method, since the numerator should be the basic radical if we are to call the ratio basicity. Experience seems to have shown the value of the limits of strength for analytical dilutions suggested in the proposed method, since the adoption of these averts several of the possible difficulties alluded to by Mr. Little in his paper in

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the February number. Two grams of sodium peroxide is ample in such a case, and since an excess does no harm, it is convenient to measure the quantities roughly by estimation in a spoon or on a spatula. The precaution of transferring to a stoppered flask to avoid loss of iodine is entirely unnecessary, since if the liquor is within the proposed limits of strength the amount of iodine liberated is much too small to suffer appreciable loss from 50 cc. or so of solution.

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## THE ANALYSIS OF TANNERY LIME LIQUORS.*

*By Hugh Garner Bennett, M.Sc., F.C.S.*

The London Conference (1912) of the I. A. L. T. C. adopted provisionally certain standard methods for the analysis of lime liquors based upon the suggestions of the Committee appointed by the Association, and the thanks of the Association are due to this Committee and to Mr. J. T. Wood in particular for the work done on the subject. A similar Committee of the American Leather Chemists' Association has recently (*J. A. L. C. A.*, 1915, p. 252), made a similar report. The provisional methods suggested, however, seem open both to criticism and to improvement. The author ventures, therefore, to give herewith a few analytical processes and suggestions which he has found useful in his own laboratory.

### I. The Estimation of Alkalinity.

The determination of the total alkalinity of lime liquors seems to present a problem not hitherto satisfactorily solved. The chief difficulty in determining the alkalinity of lime liquors has been to find a suitable indicator. Methyl orange is the most suitable indicator, as a rule, for alkalinity determinations, but it is so exceedingly sensitive to alkalies that it is even affected to some extent by the peptone matters derived from the hide by the action of lime. The end-point, in consequence, is not sufficiently sharp. Phenolphthalein can be used, but the results cannot be satisfactory because of the ammonia present,—a point apparently overlooked by the American Committee. Either, or

* *Collegium*, (London Edition), 1915, pp. 258-66, 313-22 and 329-35.

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both these indicators, however, may be used for rough control work, though in the case of sulphide limes and phenolphthalein the titration of the lime liquor must be carried out in a considerably diluted solution to avoid the escape of hydrogen sulphide.

A proposal of the writer's (*J. S. C. I.*, 1909, p. 292) to use both these indicators seems to have received more attention than it deserved. In proposing it, it was pointed out that the phenolphthalein result was inaccurate and the methyl orange result uncertain. Under such circumstances, therefore, the process can scarcely be dignified as an analytical method of any great value or significance. Nevertheless, for rough control work—in which very frequently the chief object is simply to find out whether or not a lime liquor ought to go down the drain—this process has had in the past a certain utility on account of its ease of execution. The phenolphthalein gave roughly the caustic alkalinity, and the methyl orange gave roughly the total alkalinity, the difference represented approximately the weak alkalies originating from the decomposition of the nitrogenous matters derived from the hides. In one set of lime liquors indeed, in which no sulphide, soda, or caustic soda was used, this difference was found to be proportional to the total nitrogen as determined by Kjeldahl's method, so that by a factor one could calculate approximately the Kjeldahl result from the titration difference. It was pointed out by the author in the same paper that this factor applied only to the particular set of liquors in question, and that in other yards different conditions would obtain. It was also pointed out that the factor could not be applied if sulphide were present. Moreover, with such approximate end points to the titrations it could scarcely be expected that such a factor could be generally applicable. Nevertheless, the chairmen of both Committees have been at pains to criticise the process on these very grounds! The process never claimed to be anything but useful in rough control work, where detailed analyses were impossible owing to lack of time. It is hardly worthy of more criticism or defense, but an explanation is given later (Part VI).

For more accurate determinations of the caustic alkalinity of lime liquors, alizarin paste was suggested by the writer some years ago as a suitable indicator for direct titrations. Alizarin

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is a peculiarly suitable indicator in that it is at the same time very sensitive to weak acids (cp. phenolphthalein), and also quite suitable and accurate for the estimation of ammonia. If used for the determination of the alkalinity of a lime liquor, caustic lime, any caustic soda, and the ammonia are thus titrated, the indicator being unaffected by the weakly alkaline nitrogenous matters and yet sensitive to the weak acids present as lime salts. Two precautions are necessary with its use. In the first place, as the lime salt of alizarin is insoluble it is necessary to add the indicator only near the end of the titration. If 10 cc. lime liquor are being titrated with N/10 HCl, 4 cc. acid may be usually added before the indicator. Another way is to add 1 drop of phenolphthalein and add the alizarin when the pink color is about discharged. The other precaution is necessary for sulphide limes. The 10 cc. lime liquor must be diluted considerably to prevent the escape of hydrogen sulphide, and even with the diluted liquor it is necessary that the addition of the N/10 acid and the subsequent mixing should be carried out with care to prevent the escape of this gas.

$$Na_2S + H_2O = NaOH + NaSH.$$

As sodium sulphide hydrolyzes in accordance with the above equation, *half* the soda added as sulphide is determined in this titration, in addition to the other caustic alkalies. The end point is at least as sharp as any other indicator, and alizarin is the only indicator which can be used for direct titration to yield results of any theoretical significance. Results by all other indicators yet suggested are either uncertain or empirical.

The I. A. L. T. C. Committee recommend the use of methyl red for titrating the alkalinity of lime liquors, and this was adopted in the provisional method. This yields the same results as alizarin, in the case of lime liquors which contain no sulphide, and in such cases it is perhaps advantageous in that it is more convenient and its color change is a trifle sharper. Where sulphide is present in the lime liquors, however, the use of methyl red is quite unsatisfactory. It should be realized that methyl red is not a sort of methyl orange with a sharper color change. Methyl red is quite a different indicator changing color at a hydrion concentration $10^{-6}$ to $10^{-7}$ normal, whereas methyl

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orange requires a hydrion concentration of $10^{-4}$ normal. Thus methyl red is more analogous to litmus, or cochineal, and is affected to some extent by weak acids, such as carbonic acid, hydrogen sulphide, boric acid, etc. Hence methyl red cannot be used to titrate alkali carbonates or sulphides except in boiling solution when the acid gases are driven off. In sulphide limes, therefore, methyl red is inadmissible for titration with N/10 HCl, the end point being meaningless. Indeed, if a sulphide lime liquor is titrated to a distinct red, and stirred vigorously, or shaken, the escape of the hydrogen sulphide causes the yellow color to return. It is equally futile to titrate in boiling solution as ammonia will be lost to an indefinite extent. As such a large proportion of lime liquors in these days contain some sulphide, the standard method of the Committee can scarcely justify its *raison d'être* as such, though, doubtless, the method is of value for light leathers and other cases where no sulphide has been used.

Experiments in the author's laboratory have shown that either of the two following methods are suitable for determining the total alkalinity of sulphide lime liquors. The methods are, of course, equally applicable to all lime liquors, whether containing sulphide or not, and either or both could be adopted as standard methods for total alkalinity. The two methods, though differing somewhat in principle, have been found to give the same results, so that one can be usefully employed as a check upon the other.

(1) In one method the alkalinity is determined indirectly by boiling the lime liquor with excess of standard sulphuric acid till the hydrogen sulphide is expelled, and then titrating the excess of acid.

Twenty cc. N/10 $H_2SO_4$ are pipetted into a 6-inch porcelain basin and 10 cc. filtered lime liquor are then pipetted into the acid. The mixture is diluted to about 60 cc. with distilled water and then boiled vigorously for 2-3 minutes, stirring constantly with a glass rod. The burner is then removed, and after adding any distilled water that may be necessary to make the volume about 30 cc. the liquor is titrated with N/10 caustic soda. Either methyl red or alizarin may be used as indicator, the same results being obtained. The feeble organic acids combined with lime



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which might be expected to have affected the alizarin, are either precipitated by the sulphuric acid or combined feebly with it in their amphoteric capacity of feeble bases. Possibly some are volatilized. As the lime combined with these acids is estimated in this process, the results are to that extent greater than those obtained by the direct titration of caustic alkalinity with N/10 HCl and alizarin as suggested above. The author has not found duplicate titrations to differ by more than 0.1 cc.

(2) In the other method the alkalinity is determined directly, but the liquor is first treated with excess of boric acid, which precipitates much of the peptone matters held in solution by the lime and other alkalies. These compounds are the chief cause of the poor end point obtained with methyl orange. The filtrate is titrated with N/10 acid and methyl orange, which indicator is unaffected by the excess of boric acid or by the hydrogen sulphide liberated from sulphide limes. The end point with this indicator is much better under these conditions, and the results obtained agree within 0.2 cc. with one another and with the previous indirect method. The exact procedure is as follows:

About 100 cc. distilled water and about 6 grams pure boric acid are placed in a 200 cc. graduated flask and heated on the water-bath till the acid is dissolved. Fifty cc. of the filtered lime liquor are then pipetted into the flask, which is kept for a few minutes longer on the water-bath until the nitrogeneous precipitate flocculates. The flash and contents are cooled to 15° C. under the tap, and the liquor made up to mark. A drop or two of petroleum ether will break up any froth. The liquor is then mixed, filtered, and 40 cc. filtrate (corresponding to 10 cc. of the original lime liquor) are then titrated with N/10 acid and methyl orange in a 6-inch porcelain basin.

It may be of some interest to give an actual illustration of figures obtained by these methods on a very old sulphide lime liquor. Direct titration of 10 cc. filtered liquor by N/10 HCl with methyl red (provisional standard method) gave a result which might be anything between 5.9 and 6.2 cc. With methyl orange the result was 7.0 to 7.5 cc. The two methods for total alkalinity just described gave the following results:

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| Indirect method | No. of cc. N/10 HCl required per 10 cc. lime liquor | Direct method | No. of cc. N/10 HCl required per 10 cc. lime liquor |
|---|---|---|---|
| 1st Experiment, methyl red .. | 7.0 | 1st precipitation (triplicate titrations) | 7.0, 7.0, 7.0 |
| 2nd " " " .. | 6.9 | | |
| 3rd " alizarin..... | 6.9 | 2nd precipitation (duplicate titrations) | 7.0, 7.0 |
| 4th " " ..... | 7.0 | | |

Another point in the standard method is that the lime liquor is to be filtered through "S and S 605 filter paper." As this is not now available it may be of interest to record that "Postlip Mills filter paper No. 633 D" or "Whatman No. 5" are equally suitable for the purpose.

## II. The Estimation of Ammonia.

In the determination of ammonia in lime liquors the distillation method is preferred by nearly all workers. Now, in addition to ammonia a lime liquor contains nitrogenous matters in all stages of hydrolytic decomposition, including amines and other compounds just at the point of decomposition into ammonia or amines. In simple distillation, therefore, constant results cannot be obtained, for as long as one boils the liquor some ammonia or amines are given off. The distillation must be stopped at some quite arbitrary point. In operating the Kjeldahl method 15 minutes' distillation is sufficient to drive off all the ammonia, so that in distilling ammonia from lime liquors in the same apparatus the writer has been in the habit of distilling 15 minutes and no more. The hydrolytic action during boiling is thus limited in time and approximately constant results are obtained. It is clear, however, that during that 15 minutes such hydrolysis has been taking place, and that results will be in consequence higher than the actual ammonia-amine content before the distillation. To reduce this further liberation of ammonia to a minimum, the I. A. L. T. C. Committee, following a suggestion of Procter's, recommend that HCl be added first until the liquor is acid to methyl orange, then excess of magnesia, and the liquor distilled. This in effect makes the liquor neutral except for the slight alkalinity due to the solubility of magnesia. The magnesia, however, is sufficiently strong an alkali to drive off all the ammonia from the ammonium salts formed in the neutralization. This

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suggestion has also been commended by the American Committee, but the writer has found it more uniform as well as more convenient to adopt the original suggestion of Procter, which was simply to add magnesium sulphate to the lime liquor in the form of a 10 per cent. solution. Procter suggests (*L. I. L. B.*, *p.* 63) 2-3 cc. 10 per cent. magnesium sulphate for 100 cc. lime liquor, but the author has found this quantity scarcely sufficient for the purpose. Nearly 6 cc. 10 per cent. $MgSO_4$, $7H_2O$ solution are needed for 100 cc. of saturated lime solution if all the lime is to be converted into $Mg(OH)_2$, and where sulphides, ammonia, and possibly caustic soda are also present, more will be necessary. Twenty cc. 10 per cent. $MgSO_4$, $7H_2O$ solution will, however, usually be found sufficient. In this way no useless excess of magnesia is obtained, such as is liable in the case of the acid, methyl orange and magnesia neutralization. Moreover, magnesia, unless quite freshly calcined, always contains some carbonate, and in neutralizing the excess hydrochloric acid some carbonic acid is evolved, and eventually may find its way into the distillate, causing discordance unless the right indicator be employed.

It does not seem to have been recognized that the magnesium salt has a further effect in addition to reducing the hydrolysis due to the alkalinity. Lime liquors contain a quantity of nitrogenous matters which are held in solution by the lime and which are insoluble in neutral or slightly acid solution. The use of magnesium sulphate causes these substances to be precipitated, and so less liable to hydrolytic action. Further, their precipitation makes it possible to boil the rest of the liquor without any trouble due to frothing. It is true that trouble due to frothing is reduced by adding a few drops of turpentine or a piece of paraffin wax before the distillation, but the turpentine distills with the ammonia and the paraffin wax makes an unnecessary mess of the apparatus. The use of magnesium sulphate would be justified as a froth preventer, apart from its neutralizing and precipitating effects. Indeed, the author is of the opinion that its beneficial action in reducing hydrolysis due to alkalinity may have been exaggerated, for however carefully the solution be neutralized, the hydrolytic action of the boiling water still remains.

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Moreover, it is known that even magnesia will liberate ammonia from amides, *e. g.*, carbamide.

Another point in the distillation of ammonia from lime liquors, which apparently has not been noted by the I. A. L. T. C. Committee, is that with sulphide limes it is not permissible to use the indicators, which are considered best in Kjeldahl work, *viz.*, methyl red and carminic acid. This is because hydrogen sulphide is given off as well as ammonia, and is largely retained in the distillate. A solution of sodium sulphide is generally understood to hydrolyze into caustic soda and sodium sulphydrate, but, as it usually possesses a distinct odor of hydrogen sulphide it is probable that there is a slight further hydrolysis of the sulphydrate into caustic soda and free hydrogen sulphide. Thus, hydrogen sulphide is given off on boiling and replaced by further hydrolysis. Similarly a sulphide lime liquor gives off hydrogen sulphide on boiling, as is readily shown by lead acetate paper as well as by the odor. When magnesium sulphate is present also this evolution occurs even more readily, the sulphydrate acting in hot solution in a manner quite analogous to caustic soda in the cold, thus:

$$MgSO_4 + 2NaOH = Na_2SO_4 + MgO + H_2O$$
$$MgSO_4 + 2NaSH = Na_2SO_4 + MgO + H_2S$$

In the distillation of a sulphide lime with magnesium sulphate, therefore, hydrogen sulphide is evolved even before the ammonia commences to distil, and the distillate (and laboratory) smell unmistakably of the gas. Tests of the distillate with lead acetate and nitro-prusside solutions will confirm this,—if necessary. For this reason methyl orange must be employed as indicator in titrating the distillate.

Arising partly from this is a further point. As methyl orange is to be the indicator there is no reason why the estimation of the ammonia in the distillate should be indirect. L. W. Winkler has shown (*A.* 1913, *ii*, 527, also *Zeits. angew. Chem.* 1914, 27, 630; and 1915, 28, 48), that in the Kjeldahl process the ammonia can be collected in excess of pure boric acid and then titrated direct with N/10 hydrochloric acid and methyl orange. Amines have been shown to be similarly retained and correctly estimated.

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The process is based upon the fact that boric acid does not affect methyl orange, and the author has found this suggestion very suitable in the case of the ammonia and amines evolved in distilling lime liquors, and he much prefers it to the indirect method of collecting in standard acid and titrating the excess. The boric acid method only requires one standard solution, *viz.*, N/10 hydrochloric acid, so that the indirect method is a needless complication.

The provisional method recommends that the lime liquors should be filtered through cotton wool before distillation. This seems not only unnecessary but also liable to cause discordance through loss of ammonia. The author has found it better to take the sample in a stoppered flask, and after allowing it to settle for a short time, to pipette the supernatant liquor directly into the magnesium sulphate in the distilling flask. For the actual distillation the compact apparatus described in *Collegium*, 1914, p. 482; (this J., 1914, pp. 394-397), is very convenient, and is invariably used by the writer.

Summarizing these various points, it is recommended that in determining the ammonia in lime liquors, the procedure should be as follows:

Fifty cc. of a 3 per cent. solution of pure boric acid are pipetted into the 300 cc. conical flask used as receiver, which is then placed so that the delivery tube dips into this solution. About 75 cc. distilled water and 20 cc. 10 per cent. magnesium sulphate solution are placed in the liter distilling flask, and 100 cc. of the settled lime liquor is pipetted into this solution. The flask is immediately connected up with the spray trap and the distillation commenced. After boiling vigorously for exactly 15 minutes, the receiver is removed, and its contents titrated with N/10 hydrochloric acid and methyl orange.

With this procedure results of satisfactory concordance can be obtained with any liquor. The older the liquor, however, the worse the concordance, and the greater is the necessity for adhering strictly to the stipulated 15 minutes boiling. Some actual experimental results will illustrate this.

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| Liquor | Experiment | Length of distillation minutes. | cc. N/10 HCl required |
|---|---|---|---|
| Old lime | 1 | 15 | 12.0 |
| " | 2 | 15 | 11.9 |
| " | 3 | 20 | 12.2 |
| " | 4 | 20 | 12.4 |
| Medium lime | 1 | 15 | 5.9 |
| " | 2 | 15 | 5.9 |
| " | 3 | 22 | 5.9 |

There is another possibility which should be considered in connection with the estimation of ammonia by distillation. The above experiments with an old lime indicate that an extra 5 minutes boiling releases the equivalent of about 0.3 cc. N/10 ammonia by hydrolysis even in a solution made neutral by magnesium sulphate. As in the first 5 or 10 minutes boiling, this hydrolysis will probably be taking place at an even greater rate, owing to the greater quantity of nearly hydrolyzed substances, the difference between the experimental result and the actual original ammonia content will still correspond to about 1 cc. N/10 ammonia. This indicates that although we may obtain concordance by the above method we have scarcely attained accuracy. Another alternative therefore presents itself, *viz.*, to endeavor to estimate in this distillation process not free ammonia only, but also all the ammonia which is loosely combined, and whose gradual liberation is the chief cause of error. If the lime liquor were distilled, not in neutral solution, but in strongly alkaline solution, the loosely combined ammonia would tend to be all included. Instead of trying to reduce this hydrolysis to a minimum, as in the magnesium sulphate neutralization, the hydrolysis would tend to completeness. The chief difficulty is that the same alkaline action which completes the hydrolysis of amino compounds into ammonia, is at the same time converting peptones into amino compounds, so that (as in neutral distillation) the process is never quite complete. This difficulty, however, can be very largely overcome by two modifications, *viz.*, precipitating the peptone matters with zinc sulphate before the distillation, and limiting the decomposition of amino compounds by means of potassium permanganate.

(1.) Although magnesium sulphate causes the precipitation of much nitrogenous matter, the filtrate will still give a precipitate

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with gallo-tannic acid, with bromine and with zinc sulphate. By using a 10 per cent. zinc sulphate solution, therefore, in place of 10 per cent. magnesium sulphate solution, a more complete precipitation of nitrogenous matters is obtained, the filtrate in this case giving no precipitate with bromine water, and only a very slight precipitate with gallo-tannic acid. The mixture of lime liquor and 10 per cent. zinc sulphate is filtered, and an aliquot proportion of the filtrate taken for distillation with caustic soda. The use of zinc sulphate has the additional advantage that all sulphides are removed as zinc sulphide along with the nitrogenous matters, and the distillation is thus free from the objectionable odor of escaping hydrogen sulphide. Further, zinc sulphate has a distinct acid reaction and if the settled lime liquor be pipetted directly into the zinc sulphate solution, errors due to the escape of ammonia are reduced to an absolute minimum. (It should perhaps be mentioned that zinc sulphate cannot replace the magnesium salt for distillation in neutral solution, as the zinc-ammonia complexes are not completely decomposed by boiling water.)

(2.) Wanklyn has shown that nitrogenous organic matter when boiled with alkaline permanganate solutions, yields up a definite portion of its nitrogen as ammonia. Hence, it has been found advantageous to introduce a considerable excess of potassium permanganate as well as of alkali into the distillation process. The results then obtained have not only a more definite significance but are also much more concordant; indeed the concordance is better under these conditions than in distillation from neutral solution. It may be objected that the distinction here drawn is still somewhat arbitrary and empirical, but this criticism can be applied equally to all methods yet suggested for distinguishing any parts of the nitrogeneous matters of lime liquors.

The procedure found most suitable for this estimation of free and loosely combined ammonia is as follows:

Fifty cc. 10 per cent $ZnSO_4$, $7H_2O$ solution are pipetted into a flask, and 200 cc. of the settled lime liquor are pipetted into this solution. After mixing well the liquor is filtered. About 100 cc. distilled water, and 50 cc. of a saturated (6¼ per cent.)

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potassium permanganate solution are placed in the distilling flask and 125 cc. of the filtrate (corresponding to 100 cc. original lime liquor) are also pipetted into the flask. Twenty grams pure caustic soda are added to the flask in solid form, and the flask immediately connected up. The liquor is warmed up until the caustic soda is dissolved, and the distillation is continued, boiling for 20 minutes. The ammonia is collected in 50 cc. 3 per cent. boric acid solution and titrated with N/10 hydrochloric acid and methyl orange.

The following results illustrate what may be obtained from a very old lime liquor, using both the above methods of distillation. The influence of the time of distillation is also illustrated for the zinc-permanganate process.

| Method | Exeriment | Time of distillation in minutes. | cc. N/10 HCl required |
|---|---|---|---|
| $MgSO_4$ and neutral ..... | 1 | 15 | 12.5 |
| | 2 | 15 | 12.4 |
| $ZnSO_4$, $KMnO_4$ and alkaline ..... | 1 | 15 | 18.8 |
| | 2 | 20 | 19.0 |
| | 3 | 25 | 19.0 |

If a complete analysis of a lime liquor is desired, it is advantageous to use both these processes, for each is devised to yield different information. If a standard method is desired the permanganate process is preferable, as better concordance would probably be obtained in different laboratories than by the neutral distillation.

### III. The Estimation of Sulphide.

It has been pointed out by Blockey and Mehd (*Collegium*, 1912, p. 300; this J., 1912, pp. 358-367), that the solution of zinc sulphate and ammonia usually employed for the estimation of sodium sulphide is inapplicable in the case of lime liquors on account of the precipitation of zinc hydrate by the action of the lime, and they have proposed to avoid this by the addition of 5 per cent. ammonium chloride, as well as the ammonia to the standard zinc solution. McCandlish and Wilson (*Collegium*, 1913, p. 80; this J., 1913, pp. 28-33), though agreeing with the faultiness of the zinc-ammonia solution have criticised the process of Blockey and Mehd, partly from a misunderstanding that the ammonia was to be omitted, but partly also on the ground that

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if it were included it tends to form an error owing to the suppression of the $Zn^{II}$ ions, the concentration of which determines the precipitation of the zinc sulphide. Indeed McCandlish and Wilson have found that if there be a sufficient excess of ammonia the zinc ion can be suppressed to such an extent that no precipitate of zinc sulphide will be obtained. Blockey and Mehd (*Collegium*, 1914, 75; this J., 1914, pp. 176-189), have pointed out the misunderstanding as to the omission of ammonia in their reagent, and have admitted also that a solution with a "large excess of ammonia cannot be used for the estimation of sulphides." Apparently Blockey and Mehd are of the opinion that if just enough ammonia be added to re-dissolve the zinc hydrate (before adding the ammonium chloride) sufficient ammonia will then be present to prevent the escape of hydrogen sulphide, but not sufficient to suppress the zinc ion to such an extent that an error will be caused through the non-precipitation of zinc sulphide. It is quite possible that this assumption is usually correct, both for sodium sulphide solution and for lime liquors, but it is by no means certain that this will invariably be the case.

All these workers speak of adding ammonia to zinc sulphate until the precipitate is re-dissolved as if that represented a perfectly definite amount of ammonia. This is not so! If ammonia be so added and the solution diluted, zinc hydrate is reprecipitated, and at that dilution very much more ammonia is required.* Hence, if any worker makes up his solution according to Blockey and Mehd, the amount of ammonia he uses may vary within very wide limits, according to the amount of liquid in his liter flask before adding the ammonia. To determine the amount of ammonia required it is necessary to settle at what dilution of zinc sulphate the ammonia should be added. Should one dissolve in as little water as possible and add ammonia till clear, or should one dilute to (say) half-a-liter before adding ammonia? There will be an enormous difference in the amount of ammonia

* EDITORS' NOTE.—Mr Bennett evidently has not seen the paper by Messrs. Mc Candlish and Wilson in this Journal, 1914, pp. 203-7, in which the point here made in regard to the concentration of the solution when the ammonia is added is taken up, p. 205. The same conclusion in regard to the proper amount of ammonia to add is reached by Mr. Bennett as by Messrs. McCandlish and Wilson.

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required for the two cases. Now McCandlish and Wilson have made clear the desirability of avoiding a great excess of ammonia, and it would seem that a much smaller quantity of ammonia than might be involved by the procedure of Blockey and Mehd, would be the best to ensure the maximum accuracy. Indeed, as the ammonium chloride assists in preventing the precipitation of zinc hydrate, much less ammonia is needed than may be added by this procedure. Moreover, the author has noticed in making up this reagent under varying circumstances and dilutions that much the greater part of the zinc hydrate is re-dissolved by the earlier additions of ammonia, and that it is the solution of the last traces of precipitate which lead the operator to add excess of ammonia. This excess seems utterly unnecessary when ammonium chloride is to be added, and is positively harmful in that it suppresses the zinc ion and, in addition, oxidizes the nitro prusside indicator. It is clearly desirable, therefore, to limit definitely the amount of ammonia to be added, and by preference to have an approximately constant amount present in the reagent.

Experiments have been made with a view to determine the most suitable amount of ammonia to use in this reagent. In making up the reagent according to Blockey and Mehd, as much as 250 cc. concentrated ammonia may be sometimes added per liter, which would make the solution about 5 N in ammonia. The author has found one-tenth of this to be sufficient, *i. e.*, to have the reagent N/2 in ammonia approximately. It may appear that even this amount of ammonia is unnecessarily large, but it must be remembered that all such solutions will precipitate zinc hydrate on dilution, and even at this strength, a *few drops* of the reagent will give a turbidity if added to a few cc. water. If, however, 1 cc. of such reagent be added no precipitate is obtained, as the amounts of ammonia and of ammonium chloride entering along with the reagent are sufficient to ensure the zinc hydrate being re-dissolved or kept in solution.

An alternative plan seemed to lie in the addition of an ammonium chloride solution to the sulphide solution or lime liquor before titration, but this proved impracticable on account of the escape of hydrogen sulphide. A solution of sodium sulphide

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smelling faintly of hydrogen sulphide, yields a much more pronounced odor of the gas if a solution of ammonium chloride be added. This is doubtless due to the hydrolysis of the ammonium sulphide formed in double decomposition. This alternative plan was abandoned in consequence, but the fact is recorded here, in order to point out that there is danger in a too great excess of ammonium chloride as well as in a too great excess of ammonia.

In view of these various considerations the author has found that the standard zinc solution is best made up as follows:

Fifty grams ammonium chloride and 14.35 grams of $ZnSO_4$, $7H_2O$ are both dissolved completely in about 500 cc. distilled water in a graduated liter flask, and 25 cc. concentrated ammonia (SG.880) are then added. No precipitate is obtained. The solution is made up to mark 15° C.

The nitro-prusside indicator is certainly much less cumbrous than the lead acetate indicator, but it is insensitive to any hydrolyzed sulphide and very readily oxidizes owing to the ammonia. The writer very much prefers to either of these a 1 per cent. solution of nickel sulphate (Sutton, *Vol. Analysis,* 10th Ed., p. 342), spotted on a white tile. A black precipitate is obtained if any sulphide is still unprecipitated by zinc, and a blue color is noticed when the precipitation of the sulphide is complete. This latter color is due, of course, to the action of ammonia on the nickel salt.

Experiments have been made also with a view to finding a suitable alternative method for estimating sulphides. Procter (*Leather Chemists' Pocket Book,* p. 34), suggests that the lime liquor be acidified and the hydrogen sulphide distilled into N/10 iodine solution, and the excess iodine titrated with thio-sulphate. The author has found that the most suitable way of liberating the hydrogen sulphide is by distilling the lime liquor with excess of magnesium sulphate just as in the estimation of ammonia previously described. The evolution of hydrogen sulphide was mentioned, in that connection, and W. Feld (*Dict. Chem. Ind.,* 1898, p. 372) has shown that the decomposition of alkali or alkaline earth sulphides by boiling with magnesium salts is quantitatively complete. The advantage of this procedure is that the hydrogen sulphide, coming from a liquor which is faintly alkaline, is evolved

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more steadily than if suddenly liberated by excess of acid. Moreover, the ammonia which is likewise evolved assists also to steady the liberation of the gas, as well as to secure its absorption at the receiving end of the condenser. The Kjeldahl apparatus forms a suitable distilling apparatus, but it is desirable in this case to have a trap in addition to the ordinary receiver. A suitable receiver is a 6-oz. bottle fitted with a rubber bung through which passes a glass tube to connect with the condenser, and a calcium chloride tube filled with glass wool to serve as the trap.

Sutton (*Volumetric Analysis,* 10th Ed., 347) indicates that hydrogen sulphide is better estimated by Mohr's residual method with arsenious acid, than with iodine direct. The estimation of hydrogen sulphide in coal gas is often carried out with the arsenious acid method. The writer has found this method very suitable in the present instance. The hydrogen sulphide is collected in a solution of caustic soda, and a definite excess of standard alkali arsenite solution is added. After acidifying distinctly with hydrochloric acid, which precipitates arsenious sulphide, the whole is diluted to a definite volume, filtered, and the excess of arsenious acid is estimated in an aliquot part of the filtrate by titrating with standard iodine solution.

The exact procedure recommended is as follows:

About 100 cc. distilled water and 20 cc. 10 per cent. magnesium sulphate solution are placed in the distilling flask, and 100 cc. settled lime liquor are pipetted directly into this solution and the flask immediately connected up with the condenser. The receiver contains 10 cc. N/1 caustic soda, which is added by pipetting it through the glass wool in the trap. The delivery tube from the condenser should dip into this caustic soda. The distillation is then commenced and the liquor is boiled steadily but vigorously for 15 minutes. The contents of the receiver, which will have increased in volume during the distillation, are washed carefully into a 200 cc. graduated flask, including, of course, the alkaline liquid in the trap. Into this solution 20 cc. N/10 alkaline arsenite solution are pipetted, and after adding 1 drop of methyl orange, sufficient concentrated hydrochloric acid (about 5 cc.) is added to make the liquor distinctly acid to methyl orange when mixed with a rotary motion. The orange arsenious sulphide is

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then precipitated. The liquor is made up to mark and mixed well. Some little care is here necessary as the escaping carbonic acid tends to release the stopper prematurely. The liquor is now filtered through a dry filter paper and 100 cc. of the clear filtrate is pipetted into a 300 cc. conical flask for titration. Before the titration is commenced, this liquor is made distinctly alkaline to methyl orange by the addition of a saturated solution of sodium bicarbonate. The solution is then titrated with N/10 iodine, adding a few drops of starch towards the end of the reaction. If $n$ cc. N/10 iodine be required then $(20—2\,n)$ cc. N/10 arsenious solution is the measure of the precipitated sulphide.

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$$

Hence, 1 cc. N/10 arsenious solution = 0.002557 gram of $H_2S$, or 0.018018 gram $Na_2S, 9H_2O$.

Comparative experiments with this method and the zinc sulphate method have been made and the two processes have given good agreement. An illustration is as follows:

Direct titration = 0.099 per cent. $Na_2S, 9H_2O$
Distillation = 0.106 per cent. " "

The distillation process requires somewhat more time, but is capable of a greater accuracy, owing to the superior end point. The distillation process is also much the most suitable method for liquors containing only small amounts of sulphide. In such cases the error with the end point in titrating with zinc sulphate bears too great a proportion to the total titration, leading to the large percentage of errors pointed out by McCandlish and Wilson. In cases where 100 cc. lime liquor requires less than 2 cc. N/10 zinc sulphate, the distillation process is very much to be preferred, and in the author's opinion should invariably be used.

## IV. The Estimation of Soda.

The I. A. L. T. C. provisional methods make no recommendations as to the estimation of sodium in lime liquors, and the report of the American Committee indicates that "no reasonably satisfactory method has been proposed." Procter, however, has proposed a method, upon the accuracy of which no doubts have been thrown (*L. I. L. B.*, p. 86). In this a measured quantity of filtered liquor is evaporated to dryness, ignited to destroy

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organic matter, the residue carbonated by moistening with ammonium carbonate and gently igniting. The soda is then separated and estimated "by washing the ignited and carbonated residue on a filter, and titrating the solution with N/10 hydrochloric acid and methyl orange."

Experiments in the author's laboratory have indicated this course to be quite "reasonably satisfactory," if the proper precautions be observed. It is of course essential for the accuracy of the method that the re-carbonation of the lime should be complete, and that the re-ignition should not decompose the carbonate, but the care here necessary is elementary enough. The chief disadvantage of the method is that it is a side issue in Procter's method for estimating total lime, and that if one attempts to estimate both total lime and soda in the same portion of liquor, either the amount of lime taken is too large, or the amount of soda too small. As the concentrations of lime and soda are frequently very different, it is better to make these estimations on separate portions of the liquor being tested. Further, if sufficient of the sample be taken to yield a reasonable amount of soda, the total solids are often larger than is convenient to give a quick and complete ignition, and the ignited residue is too large to wash out easily and completely the sodium carbonate.

To avoid these difficulties the author has made a practice of first precipitating the lime (together with some organic matter), by means of ammonium oxalate, and of evaporating and igniting the filtrate. In this way the ignition is much more speedily completed, and the re-carbonation and re-ignition are avoided. The evaporated residue consists of sodium oxalate, the excess of ammonium oxalate and some organic matter. The ignition destroys the organic matter and converts the sodium oxalate into sodium carbonate. The excess ammonium oxalate is first converted into ammonium carbonate and then driven off. As alkali is not easily washed out with water only, especially after ignition, is has been found an advantage to dissolve the ignited residue in boric acid. The ordinary precautions for precipitating calcium oxalate are desirable to ensure the precipitate being obtained in so coherent a form that it is perfectly retained by the filter. The

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exact procedure may be varied somewhat to suit the concentration of soda in the liquor. When the calcium oxalate is precipitated and filtered, the precipitate may be washed well and the washings added to the filtrate for evaporation and ignition. Where the amount of soda is small, however, this course necessitates the evaporation of a large quantity of liquor, and is in any case somewhat slow. For general purposes the following procedure has been found most convenient:

Into a 200 cc. graduated flask are pipetted 100 cc. filtered lime liquor and 10 cc. 10 per cent. ammonia are added. The flask and contents are heated to boiling point on the water bath. In a beaker or beaker-flask 20 cc. saturated (4 per cent.) ammonium oxalate solution and 10 cc. 10 per cent. ammonia are also heated to boiling point, and then added to the hot lime liquor. The contents of the 200 cc. flask are digested on the steam bath for 10-15 minutes, cooled to 15° C., made up to mark and mixed well. The liquor is filtered through a suitable dry filter, and 50 cc. of the clear filtrate (corresponding to 25 cc. original lime liquor) are evaporated to dryness in a platinum basin. The residue is ignited strongly, dissolved with the help of 25 cc. of warm 3 per cent. boric acid solution, washed into a 300 cc. conical flask and titrated with N/10 acid and methyl orange.

If the amount of soda present is small, another 50 cc. filtrate may be pipetted in addition after the first evaporation, and the residue of both ignited together.

If the amount of soda be very small, further 50 cc. filtrate may be taken, but in this case it will be found better and quicker to ignite after each evaporation of 50 cc., as the ignition of a large amount of solid matter at once is undesirable and sometimes difficult to complete.

If the amount of soda be so small that a titration of sufficient size is not obtained by any of the above courses, the best plan is to vary the earlier part of the method so as to avoid any dilution. For example, 100 cc. lime liquor are pipetted into a beaker flask and the oxalate precipitated as before, this beaker-flask is kept on the water bath until the contents are nearly evaporated. The liquor is then washed into a 100 cc. graduated flask, cooled,

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made up to mark, filtered, and 75 cc. filtrate may be evaporated, ignited and titrated.

## V. The Estimation of Lime.

It is in connection with the estimation of total and caustic lime that the greatest care is needed in filtering the lime liquors, which invariably contain calcium hydrate and carbonate in suspension, and Wood has shown that the latter is frequently present in such a form that it easily passes through many filter papers.

(1.) Total Lime.—The estimation of total lime presents no difficulty. It may be carried out either volumetrically or gravimetrically. The former is somewhat quicker and is quite well summarized in the report of the American Committee (this J., 1915, pp. 252-258; *Collegium*, 1915, p. 179), except that the author prefers to evaporate 25 cc. only of clear lime liquor, instead of 50 cc. as recommended by Oberfell. The advantage of the smaller quantity lies in the fact that the evaporation of the liquor, the ignition of the total solids, and the washing of the calcium oxalate precipitate, can be carried out not only in much less time, but with greater accuracy. The ignition of large amounts of solid matter, and the washing of large precipitates are both liable to incompleteness. The size of the titration with N/10 permanganate is such that no loss of accuracy is involved by using the smaller quantity.

(2.) Caustic Lime.—It is curious that the ingredient of lime liquors which can be estimated with the least accuracy is the caustic lime itself.

(i) Procter (*L. I. L. B.*, p. 85) suggests that the filtered liquor may be titrated with standard hydrochloric acid and phenolphthalein, the ammonia if not negligible being expelled by a short boiling. Experiments made to test the accuracy of this procedure have not yielded encouraging results. A used lime liquor, containing no sulphide, was filtered, and 100 cc. filtrate together with some distilled water were boiled in the Kjeldahl apparatus for 15 minutes and the ammonia collected and titrated as usual. The liquor remaining in the flask was also titrated with standard hydrochloric acid and phenolphthalein. The sum of these two parts of the alkalinity was distinctly less than the amount of



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standard acid required by the same volume of filtered liquor when titrated with standard acid and phenolphthalein direct. The inaccuracy was greater than could be explained by the use of phenolphthalein and ammonia, and there is little doubt that the chief cause is found in the neutralization of the caustic lime by the further hydrolysis of the organic matter during the boiling. It has peviously been shown that such hydrolysis takes place, and not only is caustic lime consumed in replacing the ammonia liberated during such hydrolysis, but also in forming other organic calcium salts, irrespective of any liberation of ammonia. In the presence of sulphides also the method cannot be used, some hydrogen sulphide being evolved, but not all.

(ii.) The report of the American Committee gives the following method:

"Subtract the alkalinity due to sulphides and ammonia from the total alkalinity as determined when using phenolphthalein as indicator."

This, however, is not quite so simple as it would appear. A lime liquor which has been used after adding sodium sulphide, no longer contains the sodium (Na) and sulphydrate ($SH^1$) ions in the same proportion as before use. The sodium sulphide hydrolyses into hydrate and sulphydrate of soda, and these are absorbed by the hides independently and at different rates. Thus, in such a case it is necessary not only to estimate ammonia and sulphides, but also to estimate soda. Moreover, even if it be found that the sodium and the sulphur are present in the same proportions as in sodium sulphide, it is still necessary to remember that sulphydrate is neutral to phenolphthalein, so that only half the alkalinity due to sodium sulphide should be subtracted. Further, in titrating the clear lime liquor alizarin is a more accurate indicator than phenolphthalein on account of the considerable amount of ammonia present (see Part I above), and in using either indicator with sulphide liquors care is necessary to avoid the escape of hydrogen sulphide.

If, however, all these points be borne in mind, there is certainly here one method for estimating caustic lime, albeit a little complicated. It will be found that the calculations are simplified by stating all results in terms of N/10 reagents required

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for 10 cc. liquor. Apart from the ammonia, the determining factor is the proportion of sodium and sulphur. Although their respective ions are independent, they have usually been added at the same time as a solution of sodium sulphide, so that it is legitimate to pair them together as far as can be done.

(a.) If they be present in the proportions required by the formula NaSH, there is no caustic soda present in the liquor, and no alkalinity due to sulphide to subtract from the total caustic alkalinity as determined by direct titration.

(b.) If also there be excess of sulphur, *i. e.*, more than is required by the formula NaSH, again there is no caustic soda present, and nothing to subtract from the total caustic alkalinity. This excess of sulphur must be calculated as calcium sulphydrate.

(c.) If, on the other hand, there be an excess of sodium over sulphur, *i. e.*, more than is required by the formula NaSH then this excess must be regarded as caustic soda, and subtracted (together with the ammonia) from the total caustic alkalinity, in order to yield the alkalinity due to caustic lime.

(iii.) The least accurate of all the determinations necessary for the above calculation is the direct titration of the liquor, for apart from the question of indicator there is always the liability of the hydrogen sulphide to escape during titration. The results by the above method therefore tend to be higher than the truth. As a check, another process may be employed to take the place of the direct titration. This check process is to boil the filtered lime liquor with a magnesium sulphate solution until all the ammonia and hydrogen sulphide have been expelled, to add then excess of standard acid and titrate the excess with caustic soda and phenolphthalein. The amount of standard acid required for the solution of the magnesium hydrate is a measure of the alkalies which caused the magnesia to be precipitated. These are all the hydrates and sulphydrates of lime and soda. It should be noticed that this process does not yield the same results as the direct titration of caustic alkalinity, for *all* the alkalinity due to sulphides is included in this case, whilst that due to ammonia is not involved. As an ammonia determination is unnecessary for the calculation, this method may at any rate claim to be less

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indirect, but, of course, soda and sulphide determinations will be needed as before. In this process the errors due to escaping hydrogen sulphide, and due to ammonia being titrated with an unsuitable indicator, are both eliminated. The method, however, is liable to another error which has been pointed out before, *viz.*, the further hydrolysis of organic matter and consequent consumption of alkalinity to phenolphthalein. As the boiling is done in neutral solution, this error is reduced to a minimum.

Again, the disappearance of some of the caustic alkalinity in boiling is due to the decomposition of carbamide and similar compounds, which yield amino groups as ammonia and form carbonates with the alkali

$$CO(NH_2)_2 + Mg(OH)_2 = MgCO_3 + 2NH_3$$

To this further extent, therefore, the error due to boiling can be reduced, for by boiling the liquor for a short time after adding the excess acid, the carbonic acid will be expelled, and this magnesia will be estimated, as is desired.

The process is best carried out as follows:

About 100 cc. distilled water and 20 cc. 10 per cent. $MgSO_4$, $7H_2O$ solution are placed in a ¾-liter conical flask, and 100 cc. clear filtered lime liquor are pipetted into the flask also. The contents of the flask are boiled for 15 minutes to expel all ammonia and hydrogen sulphide, and 10 cc. N/1 sulphuric acid are then added. After boiling again for 3 or 4 minutes to dissolve the magnesia and expel carbonic acid, the excess N/1 acid is titrated with N/1 caustic soda and phenolphthalein.

(iv.) In preference to any of the above methods, the author is in the habit of using another process. In this process the errors in the direct titration of lime liquors with N/10 hydrochloric acid and phenolphthalein are eliminated by means of formaldehyde.

(a) Formaldehyde reacts with ammonia, forming hexamethylene-tetramine, thus:

$$4NH_3 + 6H.CHO = N(CH_2.N:CH_2)_3 + 6H_2O$$

The hexamethylenetetramine is neutral to phenolphthalein so that if the filtered lime liquor be titrated after adding formaldehyde, ammonia neither enters into the calculation nor interferes with the end point.

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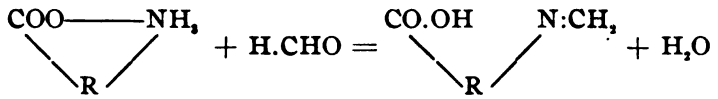
(b) Again, formaldehyde reacts with sulphydrates, converting them into hydrates, thus:

$$NaSH + H.CHO + H_2O = H.CH(OH)(SH) + NaOH$$

Hence, the alkalinity of the liquor to phenolphthalein is increased to this extent, and if the liquor be titrated after adding formaldehyde, all sulphydrates and hydrates are estimated, and there is no error due to the escape of hydrogen sulphide.

(c.) Formaldehyde reacts, however, also with the amino-acids present in the liquor (Schiff's reaction), producing acids which affect phenolphthalein, thus:



After adding formaldehyde to a lime liquor these acids are not only formed but at once neutralized by the caustic alkalies which are present in excess, so that the alkalinity of the liquor will be reduced to this extent. This reduction in alkalinity can be measured separately, however, in the manner suggested by Stiasny (*Collegium*, 1910, p. 181; this J., 1910, p. 345), and this measure is applied as a correction to the direct titration of the filtered liquor after adding formaldehyde.

The exact procedure is as follows:

First Titration.—10 cc. 40 per cent. formaldehyde solution and about 10 cc. distilled water are placed in a 300 cc. conical flask with 10 drops 1 per cent. alcoholic phenolphthalein. Decinormal caustic soda is added till a faint pink color appears; 25 cc. clear filtered lime liquor are then pipetted into this liquor and, after mixing, the liquor is titrated with N/10 hydrochloric acid until the pink color just disappears.

Correction.—To 25 cc. filtered lime liquor and 5 drops 1 per cent. alcoholic phenolphthalein in a 300 cc. conical flask, glacial acetic acid is added drop by drop until the pink color is discharged. Decinormal iodine solution is then added drop by drop until an unabsorbed excess is observed. Decinormal caustic soda is now added till the pink color just appears. Ten cc. 40 per cent. formaldehyde are neutralized to phenolphthalein as in the first titration and added to the flask. The liquor is then

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titrated with N/10 caustic soda until the pink color just reappears.

These two titrations, added together, are a measure of the hydrates and sulphydrates present in the lime liquor. If soda and sulphide determinations are made also, the caustic lime in the liquor can be calculated, as explained above. If sulphides are known to be absent there is of course no need for that determination, and the addition of iodine in the second titration is also unnecessary. The weak point in this process of estimating caustic lime is in the second titration, *i. e.*, the determination of the amino-acid correction by Stiasny's method. In this, the liquor is titrated with phenolphthalein in the presence of ammonium acetate, and the end point is, in consequence, somewhat indistinct. The error, however, is not large, and there is little doubt that the above procedure affords the most accurate way of determining caustic lime. It is noteworthy that both of the last two methods (with magnesium sulphate and with formaldehyde) first estimate hydrates + sulphydrates. The results of these two methods should therefore agree. It will be found that they do not, those by the magnesium sulphate method being, in the case of a very old lime liquor, about 10 per cent. less than those by the formaldehyde method. This is in accordance with the error already noted in the boiling of lime liquors, and is also testimony to the correctness of the formaldehyde method.

## VI. The Estimation of Nitrogenous Matters.

The estimation of total nitrogen offers no difficulty, Kjeldahl's method being used. Twenty-five cc. lime liquor are usually enough to take, unless the liquor be very new, and 10 cc. 10 per cent. sulphuric acid is sufficient to ensure acidification. It is wise to pipette the lime liquor straight into this acid, in order that no ammonia may be lost. The mixture should be evaporated down to about 5 cc. For digesting, Nihoul has shown (*Collegium,* 1915, p. 4; this J., 1915, p. 187-190) that 10 cc. concentrated sulphuric acid is quite sufficient. If permanganate is used as accelerator, the procedure suggested by Hough (*Collegium,* 1915, p. 126; this J., 1915, p. 336), enables one to obtain the acid colorless in about half an hour. If 10 cc. concentrated acid have been used, 20 grams caustic soda are ample for liberating

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the ammonia in the distilling flask. The ammonia may be received into 25 cc. N/5 hydrochloric acid and the excess titrated with N/5 caustic soda and methyl red; or may be received into 50 cc. 3 per cent. boric acid and titrated direct with N/10 hydrochloric acid and methyl orange.

It was suggested by the writer some time ago (*J. S. C. I.*, 1909, March 31), that the method of Ronchèse (*J. Pharm. Chim.*, 1907, vi, 25, 611), would prove useful to the leather chemist who wished to avoid the distillation of ammonia in Kjeldahl work. This method depends upon the fact that hexamethylene tetramine is neutral to phenolphthalein, and takes advantage of the reaction between formaldehyde and ammonia, which takes place whether the ammonia be free or present as an ammonium salt. If, therefore, the mixture of ammonium sulphate with excess sulphuric acid, obtained after the Kjeldahl digestion, be neutralized, and neutral formaldehyde added, the free acid in the liquor is an accurate measure of the ammonia previously combined with it.

In the report of the American Committee, Oberfell reports unfavorably upon this procedure, presenting figures which indicate low results compared with the ordinary Kjeldahl method. As the reaction employed in the formaldehyde process is well known, and has long been employed for quantitative work in many branches of analytical chemistry, the results of Oberfell are somewhat surprising. They admit, however, of several possible explanations.

1. They may be explained if the caustic soda used in neutralizing the excess sulphuric acid contained some carbonate. If such partially carbonated alkali has been employed, the liquor when carefully neutralized to phenolphthalein will contain not only sodium sulphate but also some sodium bicarbonate which is neutral to phenolphthalein. When formaldehyde is added and sulphuric acid liberated, this bicarbonate is neutralized during the mixing and carbonic acid escapes. Hence, in titrating the sulphuric acid is not all estimated and low results are obtained. The difficulty may easily be overcome by boiling the liquor for a few minutes just before the neutralization is complete.

2. Another possible cause of low results is that (apart from carbonization), the liquor is over-neutralized. If phenolphthalein

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be used as indicator, the appearance of the pink color is at first very faint, and unless one is somewhat familiar with the process, this point of neutrality is likely to be exceeded and more alkali used than is due. This faint color is doubtless accounted for by the presence of ammonium salts, and it is perhaps better to use methyl red for this first neutralization, and phenolphthalein for the second, after adding formaldehyde. As hexamethylene tetramine is alkaline to methyl red, the methyl red does not interfere with the observation of the phenolphthalein end point.

3. Yet another possible cause of low results would be the over-neutralization of the formaldehyde. Neutralization of formaldehyde solutions to phenolphthalein has proved ineffective when barium carbonate is used. It is necessary to add caustic soda until the phenolphthalein is just reddened. As the first appearance of pink is not very strong, the point is liable to be passed and more alkali used than necessary. This excess neutralizes some of the acid liberated by the formaldehyde and causes low results.

4. It should be noted also perhaps that if strong alkali be added uncautiously to the excess acid, heat, and a local excess of alkali may cause ammonia to escape and low results to be obtained.

5. Another cause of low results is an imperfect digestion with sulphuric acid. Amines which would be estimated as ammonia by the distillation process might not be estimated by the formaldehyde process. Such imperfect digestion is also liable to interfere with the delicacy of the end point.

6. Discordance will also arise from the use of many of the accelerators of digestion. Hough (*Collegium*, 1915, p. 127; this J., 1915, p. 336), says that after hastening the digestion with permanganate, (according to his useful suggestions) the Ronchèse reaction may be employed, but that he has found the end point very indistinct. There is little wonder when manganese salts are present! Other salts of weak bases are equally inadmissible in a method which depends upon exact neutralization. The use of potassium sulphate, however, is quite in order as an accelerator.

Operators who still have difficulty with this process should experiment with N/10 ammonium sulphate solutions, in the pres-

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ence of excess sulphuric acid, until they obtain the theoretical results. The process offers no advantage in speed over distillation, for the time gained by using permanganate is usually greater than the time lost in distillation. The advantage of the process is that no distillation apparatus is necessary; the whole operation may be conducted in one flask.

The method is certainly capable of a better agreement with the Kjeldahl process than is indicated by the results of Oberfell, and in the writer's experience generally yields nitrogen higher to the extent of a fraction of a milligram per cent. Surely this is accurate enough.

Three comparative experiments will illustrate this:

| Method | Mgms. N per 100 cc. lime liquor | Nitrogen per cent. |
|---|---|---|
| Kjeldahl | 75.1 | 0.0751 |
| Formaldehyde 1 | 75.6 | 0.0756 |
| Formaldehyde 2 | 75.8 | 0.0758 |

Oberfell is to be congratulated upon the excellent concordance in his Kjeldahl work. His best duplicates show perfect agreement to 0.00001 per cent. nitrogen. In a liquor containing free ammonia, to estimate nitrogen with an accuracy up to one part in 10 millions is sublime. The author must confess not only that he cannot do it, but also that he is more easily satisfied.

Various methods for distinguishing the different kinds of nitrogenous matters have been suggested, but none are of much practical value. The author has made a practice of dividing the nitrogenous matters in the following way: First acidifying slightly with hydrochloric acid, filtering off and Kjeldahling the precipitate; and then adding excess of gallo-tannic acid (suggested by Procter's method), and also filtering and Kjeldahling this precipitate. If then the total nitrogen and the ammoniacal nitrogen have been determined, the nitrogenous matters may be put into four classes, *viz.*:

1. Soluble in lime, but not in weak acid.
2. Soluble in lime and weak acid, but not in tan.
3. Soluble in lime, weak acid, and in tan.
4. Ammonia.

If the nitrogen so differentiated be calculated in terms of total nitrogen, it will be seen that the proportion of the various ni-

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trogenous constituents varies comparatively little in a regular system of liming. A few actual results will illustrate this point.

PERCENTAGE OF NITROGEN IN DIFFERENT FORMS.

| Age of liquor . . . . . | 2 days | 5 days | 7 days | 8 days | 11 days |
|---|---|---|---|---|---|
| 1. Soluble in lime but not in acid ..... ..... | 0.0 | 27.2 | 27.2 | 25.5 | 27.1 |
| 2. Soluble in lime and acid but not in tan ..... | 45.6 | 33.7 | 30.1 | 29.5 | 30.7 |
| 3. Soluble in lime, acid, and in tan ..... | 27.9 | 13.6 | 17.9 | 20.5 | 17.0 |
| 4. Ammonia..... | 26.5 | 25.5 | 24.8 | 24.5 | 25.2 |
| Total ..... | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

The conclusion to be drawn is that whatever the age of the lime liquor, the nitrogenous constituents are roughly in the same average state of decomposition. There is nothing particularly surprising in this conclusion, for proteid matters are continually going into solution, breaking down into peptones, further into amino compounds, and finally into ammonia, which last is continually escaping into the air. In a regular system of liming such results and such a conclusion might be expected. As, moreover, some of these nitrogenous matters are derived from the gelatinous hide, some from its keratinous covering, some from the albuminous blood and lymph, whilst some are from adhering dung, there seems little use in such differentation of nitrogenous matters, except that their increasing amount in any liquor, in approximately constant proportions, is evidence of regularity in the method of liming.

In this connection it may be pointed out that in the above results the ammonia especially bears an almost constant ratio to the total nitrogen, and hence, may be taken as indicative of the total nitrogenous matters. This means that if one determines the ammonia in a lime liquor, one can calculate approximately from it, the total "dissolved hide substances." For control work in which complete analyses cannot be made, this fact is of considerable utility.

This average constancy of composition in the nitrogenous matters is doubtless the explanation why in direct titration, the difference between the results with phenolphthalein and methyl orange were found to be approximately proportional to the total

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nitrogen, for that difference is due to weak organic alkalies which are alkaline to the same average extent. There is thus very good reason for the existence of the "factor" found by the author, although this factor will doubtless vary with different systems and in different factories. It is quite analogous to the factor by which ammonia results may be calculated roughly into total nitrogen results, as illustrated above. Wood and other critics of this factor have never published experimental results showing the inconstancy of these relationships for any particular system of liming. The author is of the opinion that the production of such results would simply be evidence of a thoroughly bad system of liming.

Now it is obvious that such factors cannot be expected to be absolutely constant, even for one set of liquors. Indeed one might expect further information to be supplied by the variation of such ratios. In one particular liquor, for example, one pack of goods remained for several days, and ammonia and hide substance determinations were made, and the factor calculated for converting the former into the latter. The results were as follows:

| Age of liquor | | Factor | |
|---|---|---|---|
| 2 days.. ..... | Ammonia % | × 17.6 = | Hide substance % |
| 5 " ..... | " | × 18.1 = | " |
| 7 " ..... | " | × 18.6 = | " |
| 8 " ..... ..... | " | × 19.0 = | " |

It will be noticed that the factor tends to increase with the age of the liquor, *i. e.*, that the percentage of nitrogen present as ammonia tends to decrease. This may be explained in two ways. In the first place the addition of proteid matters to old liquors occurs at a greater rate than their decomposition, because such liquors are used for green packs which are often dirty. Again, as all liquors are alkaline, ammonia tends to escape into the air at a greater rate when present in greater amounts.

This same average state of decomposition is also the reason why the application of Schiff's reaction for estimating amino acids, as suggested by Stiasny, has proved to be of little practical value. The average percentage hydrolysis of nitrogenous matters is obtained by this process, and (as might be expected from the above considerations) in any regular system of liming it will be

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found that this is nearly constant. As the total nitrogen content increases with the age of the liquor, the amino acid content increases at about the same rate. The average percentage hydrolysis is in consequence nearly constant in any one system of liming, being usually about 90 per cent. Old lime liquors generally show an average percentage hydrolysis which is slightly less, for the reasons noted in the last paragraph. So true is this that Helfrich (*J. A. L. C. A.*, 1915, pp. 396-408; *Collegium*, 1915, p. 268), takes the amount of amino acids as proportional to the amount of dissolved hide substance in soak liquors! By his procedure, cc. N/10 NaOH (for amino acids) $\times$ 01.64 = pounds hide substance per 100 gallons.

## VII. The Estimation of Salt.

The determination of common salt in lime liquors and soak liquors is sometimes of importance, for if salted hides are being treated, there is danger not only that the concentration of salt in the soaks becomes such that its well known solvent action on hide substance becomes appreciable, but also that salt may be carried forward into the limes in which it is said to have considerable effect in preventing the plumping of the goods. For the estimation of the salt the direct titration of soak liquors with silver nitrate has been suggested, but so far as the writer is aware, no method has been proposed for the determination in lime liquors. Now it is obvious that direct titration cannot be very reliable for soak liquors, because these liquors are never neutral and the chromate indicator requires neutrality. Soak liquors are invariably alkaline with ammonia, and in these days very frequently alkaline with caustic soda, sodium sulphide, or even lime. For the same reasons the method is inapplicable to lime liquors. Moreover, if these liquors be acidified with nitric acid and made neutral by adding excess of magnesia (as suggested in the report of the American Committee), the results are still unreliable on account of the fact that they not only contain oxidizable organic matter, but very often sulphides, which are reducing agents; and it should be borne in mind that both the basic and acidic radicles of silver nitrate are very susceptible of reduction Experiments have been made, therefore, for the

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purpose of finding methods more accurate and more generally applicable, for the estimation of salt in such liquors.

1. The first method, which is the one most strongly recommended, estimates the salt indirectly. A solution of zinc nitrate is first mixed with the lime liquor. This precipitates the sulphides as zinc sulphide, and also precipitates much of the organic matter. Zinc oxide is also precipitated by the alkalies, and the liquor becomes slightly acid, owing to the hydrolysis of the excess of zinc nitrate (cp. estimation of free and loosely combined ammonia, above). An aliquot part of the clear filtrate from this mixture is then oxidized with nitric acid, a definite excess of standard silver nitrate is added, and the excess titrated with standard thiocyanate after filtering off the silver chloride.

The exact procedure is as follows:

Twenty-five cc. settled lime liquor are pipetted into a flask which already contains 25 cc. 10 per cent. zinc nitrate solution. After mixing well the contents are filtered. Into a 200 cc. graduated flask 10 cc. of the filtrate are pipetted, about 20 cc. 10 per cent. nitric acid, and about 50 cc. distilled water are then added. The mixture is heated to boiling point on a water bath and 25 cc. N/10 silver nitrate solution are pipetted into the hot liquid. On mixing with a rotary motion the precipitate of silver chloride soon collects into large particles, the presence of the excess nitric acid assisting in this direction. The contents of the flask are cooled to 15° C., and made up to mark with distilled water. After mixing, the liquid is filtered and 100 cc. filtrate are titrated with N/10 potassium thiocyanate solution.

The ferric indicator is best made by dissolving 25 grams ferrous sulphate in dilute sulphuric acid and adding concentrated nitric acid. The liquor is first warmed on the water bath and finally boiled briskly for a few minutes to expel nitrous fumes. This solution is filtered into a 250 cc. flask, cooled and made up to mark. In titration 5 cc. of this solution should be uniformly employed.

In the case of soak liquors containing more salt it may be necessary to increase the amount of silver nitrate employed, in order to ensure a reasonable excess.

2. The alternative method is a direct method in which sul-

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phides, ammonia, and some organic matter are got rid of by boiling with magnesium nitrate. The liquor is rendered neutral at the same time, just as in the estimation of ammonia. As magnesium nitrate is hydrolyzed to some extent at boiling point, there is also some oxidation of the organic matter still remaining in solution.

Twenty-five cc. settled lime liquor are diluted to 250 cc., 50 cc. of this solution are pipetted into a 300 cc. conical flask and 5 cc. of a 3 per cent. solution of magnesium nitrate are then added. The mixture is boiled for 15 minutes, which suffices to expel all hydrogen sulphide, and precipitate and oxidize much organic matter. The solution is cooled, and being neutral is titrated with N/10 silver nitrate and the chromate indicator.

In the case of soak liquors which will contain more salt, 25 cc. or 10 cc. of diluted solution should be taken for boiling and titration, diluting to about 50 cc. with distilled water. Of course it is permissible instead of adding magnesium nitrate to acidify to methyl orange with dilute nitric acid and then add magnesia, but the boiling should in this case be continued somewhat longer, and it is better *to boil* for 5 minutes before adding this magnesia. This direct method is not so quick as the indirect method described previously. It is also not so accurate, for neither the removal of the organic matter nor the oxidation of that unremoved is so complete as with zinc nitrate precipitation and nitric acid oxidation. Hence, the direct method consumes somewhat more silver nitrate and gives results slightly too high.

In conclusion, it may be pointed out that all processes described above are equally suitable for the analysis of soak liquors. In these liquors the materials employed are often very much the same as in lime liquors.

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# A BACTERIOLOGICAL STUDY OF METHODS FOR THE DISINFECTION OF HIDES INFECTED WITH ANTHRAX SPORES.*

By F. W. Tilley,

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The number of hides and skins imported into this country each year amounts to many millions. Since these come to us from all quarters of the globe, it is evident that there is danger that they will bring with them infectious material which may cause disease among animals and human beings.

On account of the great resisting power of the anthrax spore, hides and skins imported from countries where anthrax is prevalent are regarded as especially dangerous; and inasmuch as methods of disinfection which will destroy the anthrax spore may be expected to kill other organisms with ease, considerable attention has been devoted to the problem of securing a disinfectant that will destroy the anthrax spores without damaging the hides and skins. Among the numerous processes which have been suggested, that devised in 1910 by Seymour-Jones[16] ‡ has attracted much attention, while more recently the Schattenfroh[12] method has been declared by various investigators to be equally efficient and by some even more so.

As Eurich[1,2], Ponder[9,10], Seymour-Jones[16], and others have pointed out, the spores of anthrax are found chiefly in connection with blood stains, and as these, together with other material with which the spores are likely to be associated, are colloidal in nature, the problem, as Seymour-Jones expresses it, is to get at the anthrax spore "when imbedded in a gelatinous, albuminous, or other colloidal body without injury to the material or fabric to be disinfected."

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† The writer desires to express his obligations to Mr. P. F. Veitch, chemist in charge, Leather and Paper Laboratory, Bureau of Chemistry, for the work done under his direction in tanning pieces of disinfected hide, and to Dr. E. C. Schroeder, superintendent, Bureau of Animal Industry Experiment Station, for facilities afforded in carrying out the experimental work upon animals.

‡ Reference is made by number to "Literature cited," p. 91–92.

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## OUTLINE OF SEYMOUR-JONES AND SCHATTENFROH METHODS OF DISINFECTION.

Seymour-Jones[16] proposes to attain the desired result by the use of mercuric chloride and formic acid. He holds that the acid causes the hide and the various associated colloidal substances to swell, absorb water, and become soft and tender, thus furnishing favorable conditions for the action of the mercuric chloride. Under these conditions he considers a dilute solution of mercuric chloride sufficient for disinfection. After disinfection hides are transferred to a saturated solution of common salt, whereby, it is claimed, they will be shrunk and brought to the "wet salted" state. The dilutions recommended are mercuric chloride, 1 part in 5,000, with 1 per cent. of formic acid; and the time of exposure to the disinfectant, 24 hours.

One of the first workers to investigate the Seymour-Jones process was C. W. Ponder[9 10]. He found that artificially infected pieces of hide were not disinfected in 24 hours by a solution of mercuric chloride, 1 to 5,000, plus 1 per cent. of formic acid, in 4 cases out of 10 and concluded that the effective dilution of mercuric chloride lay between 1 to 1,000 and 1 to 5,000. In spite of these results he recommends the service use of mercuric chloride, 1 to 5,000, plus 1 per cent. of formic acid, on the ground that his tests were made more rigorous than was necessary to meet the conditions obtaining in actual routine disinfection. It is worthy of note that he made no attempt to neutralize the disinfectant before testing the results by cultures and by inoculation of animals. Moegle[7] and Schnürer[13] have also reported favorable results with the Seymour-Jones method.

The investigations of Sevcik[14] controvert all these favorable results. By neutralizing the disinfectant with sodium sulphide he was able to obtain living and virulent anthrax bacilli from spores treated with very strong dilutions of mercuric chlorid and formic acid, even when the time of exposure was extended to a number of days. Judging from his published results, it would require a dilution of mercuric chloride, 1 to 500, plus 1 per cent. of formic acid, to destroy anthrax spores in 24 hours. The use of sodium sulphide in this manner does not seem unreasonable, since, as a matter of fact, many tanners use this substance for unhairing

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hides. Hilgermann and Marmann[4] have obtained similar results with the Seymour-Jones method, using ammonium sulphide as a neutralizing agent.

Another method for the disinfection of hides which has recently come into prominence is the method of Prof. Schattenfroh[12], which depends upon the use of hydrochloric acid and sodium chloride. The amounts recommended for use at room temperature are 2 per cent. of the acid and 10 per cent. of the salt, with a 48-hour exposure. At higher temperatures weaker dilutions may be employed.

Gegenbauer and Reichel[3] have carried on an extensive research with this method and report entirely favorable results. They state that they consider the Seymour-Jones method inefficient on account of the low concentration of mercuric chloride and also object to its use because of the discoloration by mercuric sulphide when sodium sulphide is used for unhairing. Their statements regarding the Seymour-Jones method appear to be based upon experimental work not yet published. The favorable results obtained by Gegenbauer and Reichel with the Schattenfroh method are confirmed by the favorable results obtained by Hilgermann and Marmann[4] as the result of comparative experiments with the Seymour-Jones and Schattenfroh methods.

Sevcik's comparison[14] of the two methods is interesting, but is not fair to the Schattenfroh method, as he admits, because of the use of solutions based on the percentage of "hydrochloric acid" rather than on the percentage of hydrochloric-acid gas.

## EXPERIMENTAL WORK ON GERMICIDAL EFFICIENCY OF DISINFECTANTS.

The experimental work was undertaken primarily with a view to determining the value of the Seymour-Jones method, and for that reason this paper deals largely with work done with that method, although some attention was paid to others, especially the Schattenfroh method.

In the absence of a supply of naturally infected hides it was necessary to make the experiments upon pure cultures and artificially infected pieces of hide. Although Sevcik[14] states that naturally infected hides are better for test preparations than those artificially infected, it does not seem that the difference is



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as great as he claims. Certainly his results with naturally infected hides, where the disinfectant was not neutralized, correspond very closely to results obtained by Ponder[9] [10] with artificially infected hides.

EXPERIMENTAL PROCEDURE.

For preliminary work the Hill "rod" method[5] seemed best adapted; so this was used, with some modifications. The method as modified is as follows: Glass rods $^3/_{16}$ of an inch in diameter and 8 inches long are etched at one end, the etched portion being about 1 inch long. Cotton is wrapped about the rods near the end not etched and the rods thrust into test tubes so as to engage the cotton in the mouth of the tube. The tubes containing the rods are sterilized by dry heat (150° C.) for one hour or more. In making tests the rods are removed and the etched portion dipped into a suspension made from a culture of the organism employed and this is allowed to dry on the rod.

Rods so infected are transferred to test tubes containing the disinfectant to be tested and there exposed to its action for varying lengths of time. After exposure the rods are washed with sterile water in order to remove traces of the disinfectant and are then transferred to tubes containing bouillon or agar, which are incubated for at least 48 hours at 37.5° C. The suspension used in infecting the rods is made from the surface growth on an agar tube by rubbing up in several cubic centimeters of sterile water enough of the growth to give a suspension of approximately the same density as a 24-hour bouillon culture of *Bacillus typhosus*. For a non-spore-bearing organism the culture should be 24 hours old, while for spore-bearing organisms cultures 1 to 2 weeks old are usually the most suitable.

In making tests with disinfectants containing mercury it is advisable to dip the rods into a saturated solution of hydrogen sulphide or an aqueous solution of some sulphide before placing them in subculture tubes. In this connection it should be mentioned that media of acid reaction have been found to exert an inhibitory action upon the growth of *Bacillus anthracis* after exposure to disinfectants. For that reason the media employed in these experiments have been neutral or slightly alkaline.

A considerable number of tests by the rod method were made

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with organic matter added to the disinfectant. This was done by removing a certain portion of the total volume of disinfectant and substituting a like amount of defibrinated blood.

Inasmuch as the use of a solution of sodium chloride did not seem essential in experiments upon "naked" anthrax spores, since this salt is said by Seymour-Jones to be used in his method to reduce the swelling of the hides caused by formic acid, a common salt solution was not used in the "rod" method experiments.

### MERCURIC CHLORIDE AND FORMIC ACID.

These experiments were designed to show the germicidal efficiency of mercuric chloride ($HgCl_2$) with and without formic acid ($CH_2O_2$) and with and without the addition of defibrinated blood. In experiment 1 the rods were infected by using an agar culture 2 weeks old for making the spore suspension. Microscopical examination of the suspension showed that plenty of spores were present. Each rod was exposed to 5 cc. of disinfectant for 24 hours and was then washed in 20 cc. of hydrogen sulphide solution or sterile distilled water. The rods were then transferred to subculture tubes of exactly neutral broth and incubated at 37.5° C. for three days.

The results of the above experiment indicate that mercuric chloride, 1 to 5,000, plus 1 per cent. of formic acid, is efficient where mercuric chloride alone is not and that the hydrogen sulphide solution should be used to neutralize the disinfectant before putting the rod into subculture tubes. The result after 48 hours' exposure to 5 per cent. of phenol indicates the resisting power of the anthrax spores. The next experiments consisted of short exposures with the addition of defibrinated blood, to test the efficiency of the method of disinfecting hides prescribed in Circular No. 23 of the Treasury Department, which consisted in immersion of hides for half an hour in a solution of mercuric chloride, 1 to 1,000. The technique was similar to that described for experiment 1, except that all rods were washed with hydrogen sulphide solution and defibrinated blood was added so as to make up 10 per cent. of the volume of the disinfectant in each tube.

The results of these experiments indicated that in the presence

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of 10 per cent. of defibrinated blood anthrax spores are not destroyed in 2 hours by mercuric chloride, 1 to 1,000, without formic acid, nor by mercuric chloride, 1 to 5,000, with 1 per cent. of formic acid, but that they are destroyed by mercuric chloride 1 to 2,000, with 1 per cent. of formic acid, under the same conditions. On the other hand, anthrax spores are destroyed by mercuric chloride, 1 to 1,000, without formic acid, and by mercuric chloride, 1 to 5,000, plus 1 per cent. of formic acid, even in the presence of defibrinated blood, when the time of exposure is 24 hours.

On account of the greatly increased germicidal power of mercuric chloride in the presence of formic acid observed in the foregoing preliminary experiments, it was deemed advisable to test the germicidal power of mercuric chloride and formic acid against anthrax spores dried upon pieces of hide. The Bureau of Animal Industry (B. A. I.) strain of *Bacillus anthracis,* which was employed in the previously described "rod" method experiments, was used in infecting the pieces of hide. The results of these experiments, both by cultural methods and by inoculation of animals, were entirely unsatisfactory, the reason for this being apparently that the B. A. I. strain of *Bacillus anthracis* produced spores of comparatively low virulence and low vitality.

For this reason a culture of an entirely different strain of *Bacillus anthracis* was obtained from the Army Medical School (A. M. S.) through the courtesy of Capt. Craig, and spores of this strain were used in all further experiments. Experiments were made with "naked" spores by the "rod" method and with spores dried upon pieces of hide. The spores of the A. M. S. strain were found to be very much more virulent and resistant to the action of disinfectants, drying, etc., than those of the B. A. I. strain. The technique of these experiments was exactly the same as for those with the B. A. I. strain, except that the quantity of disinfectant per rod was made 10 cc. instead of 5 cc.

The results of these experiments and a number of other similar experiments indicated that the A. M. S. strain of *Bacillus anthracis* was much more vigorous than the B. A. I. strain, which was used in the earlier experiments, and consequently was better suited for the purpose of this work. The following experiments,

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in which pieces of infected hide were employed, were therefore carried on with spores of the A. M. S. strain.

Some of the pieces of hide were prepared by a method essentially the same as that described by C. W. Ponder[9 10], the details being as follows: The test preparations were made by cutting out pieces of hide so that each piece weighed about 2½ grams. Blood was drawn from the ear of a rabbit and a good-sized drop allowed to fall on the center of the hair side of each piece. Before clotting occurred a loopful of a suspension of anthrax spores was mixed thoroughly into the drop of blood. The loop used was 3 millimeters in diameter of 23-gauge platinum wire. The preparations so made were dried in the incubator 23 hours and then kept at room temperature until used.

In view of statements made by Otsuki[8] that spores of anthrax are injured by drying at 37.5° C., and that the best method of preparation is by drying them at 10° C., another lot of test preparations of hide was made as follows: Pieces of hide were cut to weigh about 2½ grams. On each piece a good-sized drop of blood from a rabbit's ear was allowed to fall and into this was mixed a loopful of a suspension of anthrax spores. This suspension was prepared by rubbing up in sterile water enough of the surface growth from a 15-day agar culture to give a suspension approximately equal in density to a 24-hour bouillon culture of *Bacillus typhosus*. These pieces of hide were placed in Petri dishes with raised covers and were dried for three days in a desiccator over sulphuric acid at a temperature of 10° C. and in a vacuum equal to about 6 centimeters of mercury.

Guinea pigs were inoculated with clots from pieces of hide dried by each method. In neither case were the spores found to possess sufficient vitality to infect the animals, and it seemed evident that the methods of preparation had in some way attenuated the virulence of the spores. In view of the statement made by Roos[11] that rabbit blood is bactericidal for anthrax bacilli, while guinea pig blood is not, it seemed that the lack of virulence might be due to the use of rabbit blood. Therefore new pieces of hide were prepared, using blood from a guinea pig instead of rabbit blood as before. The pieces of hide were dried for 24 hours at 37.5° C. and then kept several days at room tempera-

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ture in a dark closet. The lower drying temperature was used in later experiments. The spores in these test preparations were found to be virulent for guinea pigs, although less virulent than the original A. M. S. culture when tested shortly after it was received.

The virulence of the cultures was therefore raised by successive inoculations until a culture was obtained which killed a guinea pig in about 36 hours after subcutaneous inoculation. This culture was then employed in preparing test pieces of hide by the method above described, guinea-pig blood being used and the pieces being dried at 37.5° C. The pieces of hide so prepared were subjected to the following tests:

Each piece of hide was exposed to 25 cc. of disinfectant for 24 hours and then soaked in 25 cc. of saturated salt solution for 24 hours. At the end of that time the clots were scraped off and inoculated into guinea pigs. The results are given in Table I.

Since in experiment 10 mercuric chloride, 1 to 4,000, plus 1 per cent. of formic acid, was shown to be efficient, while mercuric chloride, 1 to 5,000, plus 1 per cent. of formic acid, was not, further tests were made with the lower dilution.

Ten pieces of hide were exposed for 24 hours to 25 cc. (for each piece) of mercuric chloride, 1 to 4,000, plus 1 per cent. of formic acid, and then soaked 24 hours in a saturated common-salt solution. The clots were then scraped off and inoculated into guinea pigs. In one instance two clots were inoculated into one animal; in all other cases only one clot was used (Table I, experiment 11).

Another experiment (Table I, experiment 12) was made in which six guinea pigs were inoculated with one clot each from pieces of hide disinfected with mercuric chloride, 1 to 4,000, plus 1 per cent. of formic acid; two guinea pigs were inoculated with two clots each from pieces similarly disinfected; and one guinea pig was inoculated with five clots from pieces of hide disinfected with mercuric chloride, 1 to 2,500, plus 1 per cent. of formic acid. As in the preceding experiments, each piece of hide was exposed for 24 hours to 25 cc. of disinfectant and soaked in 25 cc. of saturated common-salt solution for 24 hours, after which the clots were scraped off and inoculated under the skin of the guinea pigs.

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TABLE I.—INOCULATION OF GUINEA PIGS WITH CLOTS FROM PIECES OF HIDE.

*Experiment 10.*

| No. of guinea pigs | Disinfectant (25 cc.) and dilution. | Time of exposure Hours | No. of clots inoculated | Result of inoculation |
|---|---|---|---|---|
| 2 | Mercuric chloride (1:2,000) + formic acid (1 per cent.) | 24 | 1 | Both lived. |
| 2 | Mercuric chloride (1:3,000) + formic acid (1 per cent.) | 24 | 1 | Do. |
| 2 | Mercuric chloride (1:4,000) + formic acid (1 per cent.) | 24 | 1 | Do. |
| 2 | Mercuric chloride (1:5,000) + formic acid (1 per cent.) | 24 | 1 | Both died in 5 days. Anthrax. |
| 2 | No disinfectant | (*a*) | 1 | Both died in less than 48 hrs. Anthrax. |

*Experiment 11.*

| | | | | |
|---|---|---|---|---|
| 8 | Mercuric chloride (1:4.000) + formic acid (1 per cent.) | 24 | 1 | All lived. |
| 1 | Do | 24 | 2 | Died in 5 days. Anthrax |
| 2 | No disinfectant | (*a*) | 1 | Both died in 48 hrs. Anthrax. |

*Experiment 12.*

| | | | | |
|---|---|---|---|---|
| 6 | Mercuric chloride (1:4,000) + formic acid (1 per cent.) | 24 | 1 | All lived. |
| 2 | Do. | 24 | 2 | Both lived. |
| 1 | Mercuric chloride (1:2,500) + formic acid (1 per cent.) | 24 | 5 | Do. |
| 2 | No disinfectant | (*a*) | 1 | Both died in 48 hrs. Anthrax. |

*Experiment 13.*

| | | | | |
|---|---|---|---|---|
| 2 | Mercuric chloride (1:4:000) + formic acid (1 per cent.) | 24 | 1 | Both lived. |
| 2 | Do. | 24 | 2 | Do. |
| 1 | Do. | 24 | 4 | Died in 3 days. Not anthrax. |
| 1 | Do. | 24 | 4 | Lived. |
| 1 | Sodium chloride, but no disinfectant. | (*a*) | 1 | Died in 4 days. Anthrax. |
| 1 | Do. | (*a*) | 1 | Died in 5 days. Anthrax. |

*a* Not exposed.

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The apparent discrepancy between experiments 11 and 12 in connection with results obtained by inoculation into guinea pigs of clots from two pieces of hide disinfected with mercuric chloride, 1 to 4,000, plus 1 per cent. of formic acid, may be explained on the ground that the pieces used in the second experiment had been kept longer than those used in the first and had consequently lost virulence by continued drying. Even in experiment 11 it will be seen that the disinfectant exercised a marked influence on the virulence of the spores, since the guinea pig remained alive until five days after inoculation.

The results of these experiments are confirmed by the results of a further experiment (Table I, experiment 13) performed later with test preparations of a different lot. This later lot was prepared in exactly the same way as the earlier ones; but the culture used for infecting the pieces of hide was obtained from a guinea pig dying a little more than 48 hours after inoculation, while the culture used for the pieces first prepared was obtained from a guinea pig dying within 36 hours after inoculation. The difference in the vitality of the spores is clearly seen in the length of time necessary to kill the guinea pigs inoculated from the check pieces. As will be seen by reference to Table I, this time was about 48 hours for the first lot, while for the second it was from 4 to 5 days.

In order to ascertain the effect of mercuric chloride and formic acid upon hides from the standpoint of the tanner, pieces of hide about 4 by 5 inches in size and weighing about 50 grams each were disinfected by the Seymour-Jones method, using mercuric chloride dilutions of 1 to 4,000 and 1 to 2,500 plus 1 per cent. of formic acid. The proportion of disinfectant used was 10 times the weight of the hide. These were examined and tanned in the leather and paper laboratory of the Bureau of Chemistry. Immediately after unhairing, these pieces of hide were observed to be very much blackened, but after the full process of tanning this was not evident, so it appeared that the coloring matter of the tanning liquid had covered up this discoloration.

Judged solely by the results of the various experiments previously described, it might seem that the Seymour-Jones method could be accepted as suitable for the disinfection of hides, pro-

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vided that mercuric chloride in a strength of 1 to 2,500 was substituted for the recommended dilution of 1 to 5,000. However, at this stage the writer's attention was called to the work of Sevcik[14], which appeared to controvert the favorable results obtained by various workers as well as his own previous results. Sevcik concluded that it is necessary to neutralize the disinfectant carefully before attempting, either by cultural methods or animal inoculation, to ascertain whether anthrax spores have been destroyed, and that the hydrogen sulphide solution used for a short time is not sufficient to neutralize mercuric chloride plus formic acid. The neutralizing agent which he recommended was sodium sulphide, which neutralizes both the mercury and the acid. The time which he allowed for the neutralizing process was two hours.

Sevcik's contention that the mercuric chloride and formic acid used in the Seymour-Jones method should be neutralized by sodium sulphide in order to determine whether disinfection has been complete seemed reasonable in view of the fact that many tanners use sodium sulphide for unhairing hides; therefore, in order to verify his conclusions, the following experiments were undertaken:

Pieces of hide were exposed to 25 cc. of disinfectant for 24 hours, treated with 25 cc. of saturated solution of sodium chloride for one hour and with 25 cc. of a 1 per cent. sodium sulphide solution for two hours. They were then washed with sterile water.

In experiment 14 (Table II) the clots were scraped off and inoculated into guinea pigs.

The test preparations used in experiment 14 were made as follows: Pieces of hide were cut so as to weigh about 2½ grams. A good-sized drop of guinea-pig blood was allowed to fall upon the center of each piece, and, before this clotted, a loopful of a suspension of anthrax spores was thoroughly mixed in. The suspension of spores was obtained by rubbing up in sterile water enough of the surface growth of an agar culture of *Bacillus anthracis* obtained directly from the spleen of a guinea pig to give a suspension rather more dense than a 24-hour bouillon culture of *B. typhosus*. The loop employed was of No. 23 gauge platinum

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wire 3 millimeters in diameter. The pieces of hide thus infected were dried in an electric oven at a temperature of about 45° C., in order to prevent the spores from developing into vegetative forms, which would be destroyed by the drying.

TABLE II.—INOCULATION OF GUINEA PIGS WITH CLOTS FROM INFECTED PIECES OF HIDE.

*Experiment 14.*

| No. of guinea pigs | Disinfectant (25 cc.) and dilution | Time of exposure. Hours | Result of inoculation |
|---|---|---|---|
| 1 | Mercuric chloride (1:1,000)+ formic acid (1 per cent.) | 24 | Died in 3½ days. Anthrax. |
| 1 | Do | 24 | Lived. |
| 1 | Mercuric chloride (1:2,500)+ formic acid (1 per cent.) | 24 | Do. |
| 1 | Do | 24 | Died in 3½ days. Anthrax. |
| 1 | Mercuric chloride (1:4,000)+ formic acid (1 per cent.) | 24 | Died. Mixed infection. |
| 1 | Do | 24 | Died in 4 days. Anthrax. |
| 1 | Sodium chloride followed by sodium sulphide. No disinfectant | (*a*) | Died in 3 days. Anthrax. |
| 1 | Do | (*a*) | Died. Mixed infection. |

*a* Not exposed.

In experiment 15 (Table III) the test pieces of hide were prepared as follows: Pieces cut to weigh 2½ garms were placed in a rather dense suspension of anthrax spores with hair side down. After soaking in this solution for 10 minutes they were placed in Petri dishes hair side up and allowed to dry a few minutes. Then 0.1 cc. of the spore suspension was dropped on each piece and they were allowed to stand at room temperature for one hour. The pieces of hide were then dried in an electric oven at 43° C. for two days, the covers of the Petri dishes being tilted to one side. They were then kept at room temperature until used. After exposure to the disinfectant a considerable part of the hair with some of the underlying hide was scraped off and inoculated subcutaneously into guinea pigs, instead of inoculating blood clots as before. In other respects the technique was the same as for experiment 14.

Experiment 16 (Table III) was similar to the preceding, except that the pieces of hide used were dried for three instead of two days. A culture from the heart blood of a guinea pig was used in making the spore suspension.

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TABLE III.—Inoculation of Guinea Pigs with Portions of Hide.

*Experiment 15.*

| No. of guinea pigs | Disinfectant (25 cc.) and dilution | Time of exposure. Hours | Result of inoculation |
|---|---|---|---|
| 1 | Mercuric chloride (1:1,000)+ formic acid (1 per cent.) | 24 | Died in 3½ days. Anthrax |
| 1 | Do | 24 | Lived. |
| 2 | Mercuric chloride (1:2,500)+ formic acid (1 per cent.) | 24 | Both died in 5 days. Anthrax. |
| 1 | Mercuric chloride (1:4,000)+ formic acid (1 per cent.) | 24 | Died in 4 days. Anthrax. |
| 1 | Do | 24 | Died in 3½ days. Anthrax. |
| 1 | Sodium chlorid followed by sodium sulphide. No disinfectant | (*a*) | Do. |
| 1 | Do | (*a*) | Died in 2 days. Mixed infection. |

*Experiment 16.*

| | | | |
|---|---|---|---|
| 2 | Mercuric chloride (1:500) + formic acid (1 per cent.) | 24 | Both lived. |
| 2 | Mercuric chloride (1:1,000)+ formic acid (1 per cent.) | 24 | Do. |
| 2 | Mercuric chloride (1:2,000)+ formic acid (1 per cent.) | 24 | Do. |
| 2 | Sodium chloride followed by sodium sulphide. No disinfectant | (*a*) | Both died after 4 days. Anthrax. |

*Experiment 17.*

| | | | |
|---|---|---|---|
| 1 | Mercuric chloride (1:500) + formic acid (1 per cent.) | 24 | Lived. |
| 1 | Do | 24 | Died after 7 days. Anthrax. |
| 2 | Mercuric chloride (1:1,000)+ formic acid (1 per cent.) | 24 | Both lived. |
| 1 | Mercuric chloride (1:2,000)+ formic acid (1 per cent.) | 24 | Died after 6 days. Anthrax. |
| 1 | Do | 24 | Lived. |
| 1 | Sodium chloride followed by sodium sulphide. No disinfectant | (*a*) | Died after 3 days. Mixed infection. |
| 1 | Do | (*a*) | Died after 5 days. Anthrax. |

(*a*) Not exposed.

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TABLE III.—(*Continued.*)

| No. of guinea pigs | Disinfectant (25 cc.) and dilution | Time of exposure. Hours | Result of inoculation |
|---|---|---|---|
| | *Experiment 18.* | | |
| 1 | Mercuric chloride (1:250) + formic acid (1 per cent.) | 24 | Died after 4 days. Anthrax. |
| 1 | Do | 24 | Died after 6 days. Not anthrax. |
| 1 | Mercuric chloride (1:500) + formic acid (1 per cent.) | 24 | Died after 5 days. Anthrax. |
| 1 | Do | 24 | Died after 6 days. Anthrax. |
| 1 | Mercuric chloride (1:1,000) + formic acid (1 per cent.) | 24 | Died after 5 days. Anthrax. |
| 1 | Do | 24 | Lived. |
| 1 | Mercuric chloride (1:2,000) + formic acid (1 per cent.) | 24 | Died after 5 days. Anthrax. |
| | Do | 24 | Died after 6 days. Anthrax. |
| 1 | Sodium chloride followed by sodium sulphide. No disinfectant | (*a*) | Died after 5 days. Anthrax. |
| 1 | Do | (*a*) | Died. Mixed infection. |

(*a*) Not exposed.

Apparently the added duration of drying had an injurious action upon the spores. It should be noted, however, that cultures from one guinea pig were used in preparing material in experiments 14 and 15, while the test preparations used in experiment 16 were infected by a culture derived from a different animal.

The available cultures from the same source as those used in preparing material for experiments 14 and 15 were now 1 month old. In experiment 17 (Table III) one of these was used in infecting pieces of hide in the following way: Pieces of hide 2½ grams weight were soaked in a suspension of anthrax spores for 10 minutes; then 1/10 cc. of suspension was dropped on each, and the pieces of hide were dried in an electric oven at 43° C. for 24 hours and then kept at room temperature for 24 hours before use. The covers of the Petri dishes containing the pieces of hide were kept raised during all of this time.

The results of this experiment seem to indicate that cultures derived from one animal yielded spores of very great resisting power as compared with cultures from another animal. The irregularities which will be noted in experiment 17 are probably due to the age of the culture used.

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A further series of experiments having given unsatisfactory results, it was deemed advisable to undertake comparative tests of infected pieces of hide prepared by several different methods. Further experiments were thereupon made to compare the infectivity of pieces of hide dried (1) in an electric oven at 44° C. for 40 hours; (2) in an incubator at 37° C. for 24 hours (spores in blood clots); and (3) in a desiccator over sulphuric acid at a temperature of about 10° C., the desiccator being exhausted of air down to a pressure of about 6 centimeters of mercury, time of drying, 48 hours.

Of the above only those pieces dried at a low temperature proved infectious, the guinea pig inoculated dying after one week. As a guinea pig inoculated by pure culture also remained alive for a week, it seemed that the process of drying at 10° C. in a vacuum over sulphuric acid had not appreciably diminished the virulence of the spores. This process was therefore used in the preparation of all further test pieces of hide.

Previous experiments had shown a difference between the two strains of guinea pigs which had been used in these experiments, one strain being much more susceptible to infection by anthrax than the other. The comparatively low virulence of the pure culture mentioned above seemed to be due to passage through the less resistant strain of guinea pigs. Beginning, therefore, with a culture which had not been so treated, successive inoculations were made with the more resistant strain of guinea pigs until cultures of satisfactory virulence and vitality were obtained.

A lot of pieces of hide were prepared as follows: Pieces of 2½ grams in weight were washed and dried. These were infected by a suspension made from a 7-day agar culture, in the following manner: Pieces were placed in the suspension, hair side down, and allowed to soak for 10 minutes, and then 0.2 cc. of the suspension was dropped on each. These pieces were left in Petri dishes in the ice box for half an hour with covers of dishes on. At the end of that time the dishes were placed in a desiccator over sulphuric acid and the covers raised. The desiccator was then exhausted of air and put into the ice box, where it remained 48 hours at a temperature of 10° C. The pieces of hide were then removed and kept at room temperature until used.

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A guinea pig inoculated with the pure culture used for infecting these pieces of hide died in four days. Using the pieces of hide prepared as described, the following experiments were performed:

In experiment 18, pieces of hide were exposed to the disinfectant for 24 hours, followed by a saturated salt solution for 1 hour. They were then treated with a 1 per cent. sodium sulphide solution for 2 hours and washed with sterile water. Material was then scraped from the surface of each and inoculated into a guinea pig. The results are given in Table III, experiment 18.

In this experiment, as in those of similar character preceding it, neutralization of the disinfectant by sodium sulphide was done within a comparatively few hours after the process of disinfection was complete. In view of the strong dilution (1 to 250) found to be inefficient under these circumstances, no further attempt was made to find a dilution strong enough to disinfect, with neutralization afterward. Instead of this, an attempt was now made to determine how long spores remained viable after treatment of the pieces of hide by much weaker dilutions of mercuric chloride plus formic acid. This seemed worth while because the Seymour-Jones method was originally proposed to be employed at foreign ports, and in a voyage of ordinary length a considerable time would thus elapse between the time of disinfection and time of arrival at destination.

In experiment 19 (Table IV) a number of pieces of hide were exposed for 24 hours to mercuric chloride, 1 to 4,000, plus 1 per cent. of formic acid, treated with saturated common salt for 1 hour, and then laid aside and at intervals treated with sodium sulphide and inoculated into guinea pigs. In each case they were treated with 1 per cent. of sodium sulphide for 2 hours and washed with sterile distilled water. Material was then scraped from each piece and inoculated subcutaneously into a guinea pig.

The irregular results noted above might be due to variation in the extent of infection of the various pieces of hide.

In another experiment with similar technique, except that the pieces of hide were infected at a different time and by a different culture, the results were as given in Table IV, experiment 20.

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TABLE IV.—INOCULATION OF GUINEA PIGS WITH INFECTED PORTIONS OF HIDE.

*Experiment 19(a).*

| No. of guinea pigs | Disinfectant (25 cc.) and dilution | Time of exposure. Hours | Time before treatment with sodium sulphide. Days | Result of inoculation |
|---|---|---|---|---|
| 2 | Mercuric chloride (1:4,000) + formic acid (1 per cent.). | 24 | 1 | Both lived. |
| 1 | Do | 24 | 2 | Died after 6 days. Anthrax. |
| 1 | Do | 24 | 2 | Died. Pneumonia. |
| 1 | Do | 24 | 3 | Died after 6½ days. Anthrax. |
| 1 | Do | 24 | 3 | Lived. |
| 1 | Do | 24 | 4 | Died after 10 days. Anthrax. |
| 1 | Do | 24 | 4 | Died. Pneumonia. |

*Experiment 20 (b).*

| | | | | |
|---|---|---|---|---|
| 2 | Mercuric chloride (1:4,000) + formic acid (1 per cent.). | 24 | 1 | Both lived. |
| 1 | Do | 24 | 3 | Died after 6 days. Anthrax. |
| 1 | Do | 24 | 3 | Lived. |
| 1 | Do | 24 | 6 | Died after 4 days. Anthrax. |
| 1 | Do | 24 | 6 | Died after 5 days. Anthrax. |
| | | | Weeks | |
| 2 | Do | 24 | 2 | Both lived. |

*a* Control guinea pig died of anthrax in 5 days.

*b* Control guinea pig died of anthrax in 7 days.

*Experiment 21 (a).*

| | | | | |
|---|---|---|---|---|
| 2 | Mercuric chloride (1:4,000) + formic acid (1 per cent.). | 24 | 1 | Both lived. |
| 1 | Do | 24 | 4 | Died after 9 days. Anthrax. |
| 1 | Do | 24 | 4 | Died after 3 days. Anthrax. |
| 1 | Do | 24 | 9 | Died after 7 days. Anthrax. |
| 1 | Do | 24 | 9 | Died after 6 days. Anthrax. |
| | | | Weeks | |
| 1 | Do | 24 | 2 | Do. |
| 1 | Do | 24 | 2 | Died after 8 days. Anthrax. |

*Experiment 22 (b).*

| | | | | |
|---|---|---|---|---|
| 1 | Mercuric chloride (1:4,000) + formic acid (1 per cent.). | 24 | 1 | Died after 9 days. Anthrax. |
| 1 | Do | 24 | 1 | Lived. |
| 1 | Mercuric chloride (1:2,500) + formic acid (1 per cent.). | 24 | 1 | Died after 13 days. Anthrax. |
| 1 | Do | 24 | 1 | Lived. |
| 2 | Do | 24 | 2 | Both lived. |
| 1 | Do | 24 | 4 | Died after 6 days. Anthrax. |
| 1 | Do | 24 | 4 | Lived. |
| 2 | Do | 24 | 6 | Both lived. |

*a* Control guinea pig died of anthrax in 4 days.

*b* Control guinea pig died of mixed infection.

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In experiment 21 (Table IV), also, the procedure was the same as in experiment 19, except that the test pieces of hide were infected by a different culture.

Experiment 22 (Table IV) was similar to the preceding experiments, except in the use of a stronger solution of the disinfectant.

In connection with experiments 20, 21, and 22 part of the material scraped from the pieces of hide was plated out to determine whether sterilization had been accomplished. Growth of some kind was obtained in every instance, although *Bacillus anthracis* was isolated in only about one-third of the cases. In one instance *B. anthracis* was recovered from material which failed to cause anthrax when inoculated into guinea pigs, but on the other hand, one guinea pig died from anthrax after inoculation with material which failed to yield *B. anthracis* by the plate method.

### HYDROCHLORIC ACID AND SODIUM CHLORIDE.

In view of the apparent inefficiency of the Seymour-Jones method and the favorable results reported by various workers using the Schattenfroh method, experiments were now undertaken to determine the germicidal power of hydrochloric acid and sodium chloride against anthrax spores, both as "naked" spores and as contained on and in infected pieces of hide. The Schattenfroh method[12] as described by Prof. Schattenfroh consists of immersion of hides in solutions of hydrochloric acid and common salt, the proportions recommended varying according to temperature. The proportions recommended for use at room temperature are 2 per cent. of hydrochloric acid plus 10 per cent. of sodium chloride, with the time of exposure 48 hours. At higher temperatures less of the acid is needed and the time of exposure is shortened, but inasmuch as special apparatus would be needed to maintain these higher temperatures it seemed that disinfection at these higher temperatures could be disregarded as being of little practical significance.

The experiments here described were therefore carried on at room temperature. In all cases dilutions were calculated upon the percentage of absolute hydrochloric acid, not upon the percentage of "concentrated hydrochloric acid." In accordance with

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Schattenfroh's recommendations, a sodium carbonate solution was used after exposure to the disinfectant, in order to neutralize the hydrochloric acid.

A series of experiments was first made by the rod method, using various proportions of hydrochloric acid and sodium chloride. The time of exposure in each case was 24 hours, and rods were washed with a 2 per cent. solution of sodium carbonate to neutralize the hydrochloric acid. Experiment 23 was made without the addition of organic matter, with concentrations of hydrochloric acid from 1 to 5 per cent., and of salt from 5 to 20 per cent.: No growth from any one of 20 rods. Experiment 24 was made with the addition of 1 cc. of defibrinated blood to 9 cc. of disinfectant in each tube. In this case concentrations of acid of 3 per cent. or over, with 10 per cent. or more of salt were effective. An experiment upon mercuric chloride, alone and with acetic acid and formic acid was made at the same time, and with rods infected by the same spore suspension. In no case was this combination effective. In experiment 24 the hydrochloric acid rods were washed in a 20 cc. sodium carbonate solution for one minute, and the mercuric chloride rods in a 20 cc. saturated hydrogen sulphide for one minute.

In experiments 26 and 27 (Table V) are shown a comparison of hydrochloric acid and common salt with several other disinfectants, all with 24-hour exposure. Three rods were used with each dilution, showing the result, respectively, when no defibrinated blood was added, with ½ cc. of blood added to each tube and with 1 cc. of blood added to each tube. The hydrochloric-acid rods were washed with a 2 per cent. sodium carbonate solution, the mercuric chloride rods with a saturated hydrogen sulphide solution, and the formalin and carbolic-acid rods with distilled water.

The technique of experiment 27 was the same as that of No. 26. In this case two rods were used with each dilution, showing results with ½ cc. and 1 cc. of defibrinated blood.



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TABLE V.—GERMICIDAL EFFICIENCY OF HYDROCHLORIC ACID PLUS SODIUM CHLORIDE, FORMALIN, PHENOL, AND MERCURIC CHLORIDE, WITH AND WITHOUT FORMIC ACID, BY THE ROD METHOD.

*Experiment 26.*

| Disinfectant (10 cc.) and dilution | Time of exposure. Hours | Result. No blood added | Result. ½ cc. blood added | Result. 1 cc. blood added |
|---|---|---|---|---|
| Hydrochloric acid (1 per cent.) + sodium chloride (10 per cent.) | 24 | No growth. | No growth. | No growth. |
| Hydrochloric acid (2 per cent.) + sodium chloride (10 per cent.) | 24 | Do. | Do. | Do. |
| Hydrochloric acid (3 per cent.) + sodium chloride (10 per cent.) | 24 | Do. | Do. | Do. |
| Mercuric chloride (1:1,000) + formic acid (1 per cent.) | 24 | Do. | Do. | Growth. |
| Mercuric chloride (1:2,000) + formic acid (1 per cent.) | 24 | Do. | Do. | Do. |
| Mercuric chloride (1:4,000) + formic acid (1 per cent.) | 24 | Do. | Growth. | Do. |
| Mercuric chloride (1:8,000) + formic acid (1 per cent.) | 24 | Do. | Do. | Do. |
| Mercuric chloride (1:16,000) + formic acid (1 per cent.) | 24 | Do. | Do. | Do. |
| Formalin (1:50) | 24 | Do. | No growth. | Do. |
| Formalin (1:100) | 24 | Do. | Growth. | Do. |
| Formalin (1:250) | 24 | Growth. | Do. | Do. |
| Formalin (1:1,000) | 24 | Do. | Do. | Do. |
| Phenol (5 per cent.) | 24 | Do. | Do. | Do. |

*Experiment 27.*

| Disinfectant (10 cc.) and dilution. | Time of exposure Hours | Result ½ cc. blood added | Result 1 cc. blood added |
|---|---|---|---|
| Hydrochloric acid (1 per cent.) + sodium chloride (10 per cent.) | 24 | No growth. | No growth. |
| Hydrochloric acid (2 per cent.) + sodium chloride (10 per cent.) | 24 | Do. | Do. |
| Mercuric chloride (1:1,000) + formic acid (1 per cent.) | 24 | Do. | Do. |
| Mercuric chloride (1:2,000) + formic acid (1 per cent.) | 24 | Do | Growth. |
| Mercuric chloride (1:4,000) + formic acid (1 per cent.) | 24 | Growth. | Do. |
| Mercuric chloride (1:6,000) + formic acid (1 per cent.) | 24 | Do. | Do. |
| Mercuric chloride (1:8,000) + formic acid (1 per cent.) | 24 | Do. | Do. |
| Formalin (1:50) | 24 | No growth | Do. |
| Formalin (1:100) | 24 | Growth. | Do. |
| Formalin (1:200) | 24 | Do. | Do. |

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In experiment 28 (Table VI) a 2 per cent. hydrochloric acid solution plus 10 per cent. of sodium chloride was used with a 48-hour exposure, 25 cc. of the disinfectant being used for each piece of hide. After exposure the pieces of hide were soaked for 15 minutes in a 3 per cent. solution of sodium carbonate (25 cc. for each). The pieces of hide used were prepared by the method given by Ponder[9] [10] and were part of the same lot as the pieces used in experiment 14. After disinfection the clots were scraped off and inoculated subcutaneously into guinea pigs.

TABLE VI.—INOCULATION OF GUINEA PIGS WITH CLOTS SCRAPED FROM PIECES OF HIDE.

*Experiment 28.*

| No. of guinea pigs | Disinfectant (25 cc.) and dilution. | Time of exposure Hours | No. of clots used | Result of inoculation |
|---|---|---|---|---|
| 2 | Hydrochloric acid (2 per cent.)+ sodium chloride (10 per cent.) | 48 | 2 | Both lived. |
| 6 | Do. | 48 | 1 | All lived. |
| 2 | No disinfectant | (*a*) | | Died. Anthrax. |

*a* Not exposed.

TABLE VII.—INOCULATION OF GUINEA PIGS WITH MATERIAL SCRAPED FROM PIECES OF HIDE.

*Experiment. 29.*

| No. of guinea pigs | Disinfectant (25 cc.) and dilution | Time of exposure Hours | Result of inoculation |
|---|---|---|---|
| 5 | Hydrochloric acid (2 per cent.) + sodium chloride (10 per cent.) | 48 | All lived. |
| 1 | No disinfectant | (*a*) | Died in 3½ days. Anthrax. |
| 1 | Do | (*a*) | Died in 6 days. Anthrax. |

*Experiment 30.*

| | | | |
|---|---|---|---|
| 10 | Hydrochloric acid (2 per cent.) + sodium chloride (10 per cent.) | 48 | All lived. |
| 1 | No disinfectant | (*a*) | Died. Mixed infection. |
| 1 | Do. | (*a*) | Died after 5 days. Anthrax. |

*Experiment 31.*

| | | | |
|---|---|---|---|
| 8 | Hydrochloric acid (2 per cent.) + sodium chloride (10 per cent.) | 48 | All lived. |
| 1 | No disinfectant | (*a*) | Died after 4 days. Anthrax. |
| 1 | Do | (*a*) | Died after 3 days. Anthrax. |

*a* Not exposed.

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Experiment 29 (Table VII) was made as follows: Pieces of hide were prepared by soaking in spore suspension and then drying in an electric oven. Details given in connection with experiment 15 will apply to this experiment. The technique otherwise was the same as that of experiment 28. Material was scraped from the surface of each piece and inoculated subcutaneously into guinea pigs.

Experiment 30 (Table VII) was made upon pieces of hide prepared in the same way but infected with a different culture.

In experiment 31 (Table VII) the pieces of hide were prepared by soaking in spore suspension and drying them over sulphuric acid in a vacuum at 10° C. for 48 hours. As before, each piece of hide after disinfection was immersed for 15 minutes in 25 cc. of a 3 per cent. sodium carbonate solution.

In connection with experiment 31 an attempt was made to determine the efficiency of disinfection by plating out material from the piece of hide. The plates showed no growth even after three days' incubation; hence, it seemed that the hydrochloric acid and sodium chloride had destroyed the anthrax spores and all other organisms as well.

Experiments 32 and 33 (Table VIII) show comparative tests of the Seymour-Jones and Schattenfroh methods upon pieces of hide of the same lot. These were prepared by the method described under experiment 31. The greatest possible care was taken to neutralize the disinfectant, so far as the Schattenfroh method was concerned. Sodium sulphide was used both for Seymour-Jones and Schattenfroh pieces, because it seemed possible that the depilatory action of the sodium sulphide might bring up undisinfected spores from the depths of the hair follicles. A number of pieces of disinfected hide were kept several days and then treated with the neutralizing agent.

As a part of experiment 32, plates were made from the material scraped off the pieces of hide. In every instance the plates made from material treated by 2 per cent. of hydrochloric acid and 10 per cent. of sodium chloride were sterile. On the other hand, growth was observed on all the plates from material exposed to mercuric chloride and formic acid.

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TABLE VIII.—Comparison of Seymour-Jones and Schattenfroh Methods of Disinfecting Hides.

*Experiment 32.*

| No. of guinea pigs | Disinfectant (25 cc.) and dilution | Neutralizing solution and time required | Time of exposure. Hours | Result of inoculation |
|---|---|---|---|---|
| 2 | Hydrochloric acid (2 per cent.)+ sodium chloride (10 per cent.) | Sodium carbonate (2 per cent.) ½ hour. | 48 | Both lived. |
| 2 | Do. | Potassium hydroxide (0.5 per cent.) 2 hours. | 48 | Do. |
| 2 | Do. | Sodium sulphide (1 per cent.), 2 hours. | 48 | Do. |
| 2 | Mercuric chloride (1:2,500) + formic acid (1 per cent.) | Do. | 24 | Do. |
| | | Neutralization 4 days later. | | |
| 2 | Mercuric chloride (1:2,500) + formic acid (1 per cent.) | Sodium sulphide (1 per cent.), 2 hours. | 24 | Both died. Anthrax. |
| 2 | Hydrochloric acid (2 per cent.) + sodium chloride (10 per cent.) | Do. | 48 | Both lived. |

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TABLE VIII.—COMPARISON OF SEYMOUR-JONES AND SCHATTENFROH METHODS OF DISINFECTING HIDES.—(*Continued.*)

*Experiment 33.*

| No. of guinea pigs | Disinfectant (25 cc.) and dilution | Neutralizing solution and time required | Time of exposure. Hours | Result of inoculation |
|---|---|---|---|---|
| 2 | Hydrochloric acid (2 per cent.) + sodium chloride (10 per cent.) | Sodium carbonate (2 percent.), ½ hour. | 48 | Both lived. |
| 2 | Do. | Potassium hydroxide (0.5 per cent.), 2 hours. | 48 | Do. |
| 2 | Do. | Sodium sulphide (1 per cent.), 2 hours. | 48 | Do. |
| 1 | Mercuric chloride (1:2,500) + formic acid (1 per cent.) | Do. | 24 | Lived. |
| 1 | Do. | Do. | 24 | Died. Anthrax. |
| | | Neutralization 4 days later. | | |
| 1 | Mercuric chloride (1:2,500) + formic acid (1 per cent.) | Sodium sulphide (1 per cent.), 2 hours. | 24 | Died. Anthrax. |
| 1 | Do. | Do. | 24 | Lived. |
| 2 | Hydrochloric acid (2 per cent.) + sodium chloride (10 per cent.) | Do. | 48 | Both lived. |

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In this experiment, as in several of the last few experiments described in the previous discussion of the Seymour-Jones method, it will be noted that material from pieces of hide exposed to mercuric chloride and formic acid and treated shortly after completion of the disinfection with sodium sulphide failed to kill guinea pigs into which it was inoculated. On the other hand, material from pieces of hide allowed to stand for several days before using sodium sulphide caused guinea pigs to die from anthrax. It was noted that the depilatory action of the sodium sulphide was far more complete in the case of the pieces of hide which had been kept for several days after disinfection before treatment with the sulphide. The results of plating, as before mentioned, showed that disinfection was not complete; therefore it seems probable that the more extensive depilatory action of the sodium sulphide upon pieces which had stood for some time brought up from the depths of the hair follicles spores which had been practically untouched by the disinfectant. It also seems possible that there had been some development and multiplication of these uninjured organisms during the period of waiting.

It should be noted that in the preparation of the pieces of hide used in all the above-mentioned experiments particular care was taken to secure penetration of the spores into the pieces of hide. In order to accomplish this, the pieces of hide after being infected by spore suspensions were placed in closed Petri dishes and kept in the ice box for four or five hours before the drying process was begun.

As will be seen by reference to Table VII, the Schattenfroh method was entirely successful in every instance, and the results of plating showed that actual sterilization was accomplished. Experiment 33 (Table VIII) was exactly similar to the preceding experiment except that the pieces of hide used were infected by spores derived from a different culture. The method of preparation was the same as that described under experiment 31. In this experiment, as in the preceding one, the efficiency of the disinfectants was tested by plating out material from the pieces of hide. The results obtained varied from the results of experiment 32 in that a few colonies were found on two plates from

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material treated with hydrochloric acid and salt, while all other plates from similar material were sterile. One plate from material neutralized by 0.5 per cent. of potassium hydrate showed two colonies, while the other, from material neutralized by sodium carbonate, showed one colony. In none of the three was *Bacillus anthracis* the organism present. Therefore, although hydrochloric acid and salt did not accomplish actual sterilization in every instance, it did destroy anthrax spores in every instance.

Several pieces of hide about 50 grams weight each were exposed to 2 per cent. of hydrochloric acid plus 10 per cent. of sodium chloride for 48 hours and thoroughly washed with 3 per cent. sodium carbonate solution. They were then examined and tanned in the leather and paper laboratory of the Bureau of Chemistry, along with pieces of hide which had been treated with other disinfectants. This work was in charge of Mr. F. P. Veitch, and the result is shown in his memorandum on page 158.

### OTHER DISINFECTANTS.

Bacteriological tests were made with formalin and phenol, and pieces of hide treated by these disinfectants were examined and tanned in the Leather and Paper Laboratory of the Bureau of Chemistry. Without going into details it may be stated that, so far as could be determined by the limited number of tests, 2½ per cent. of formalin is efficient bacteriologically both against anthrax spores and against other organisms, while 5 per cent. of phenol is fairly efficient against non-spore-bearing organisms, but is practically useless against anthrax spores. It should be noted also that pieces of hide disinfected by formalin in 2½ per cent. solution were so seriously affected by the disinfectant that it was almost impossible to tan them, while pieces treated with carbolic acid were uninjured.

A few tests were made of the germicidal efficiency of mercuric chloride solutions saturated with sodium chloride. It was found that this combination is, if anything, not as efficient as mercuric chloride alone. This is presumably due to interference of the salt with the ionization of the mercuric chloride, as the work of Krönig and Paul[6] quite clearly indicates.

During the course of the investigations herein recorded, the writer noted considerable variations in the vitality and virulence

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of anthrax spores from different sources. It was also noted that the processes employed in infecting and drying test preparations exercised a variable influence upon the vitality of the spores. In view of these variations, it was found necessary to repeat the tests many times, and in order to test the various methods as thoroughly as possible, every effort was made to maintain at the highest possible point the vitality and virulence of the spores used in test preparations and to make sure of the presence of a considerable number of such spores upon each test preparation.

It seems likely that anthrax spores occurring upon naturally infected hides might in many cases be present in much smaller numbers and possess far less vitality and virulence than those used in the experiments. However, in view of the results obtained by Sevcik[14] and others working with naturally infected hides, it is evident that the spores upon such hides frequently possess very high vitality and virulence. Therefore it seems that the only safe rule to follow is to use only such disinfectants and such methods of disinfection as have been found efficient against spores of maximum vitality and virulence.

## SUMMARY AND CONCLUSIONS.

(1) THE SEYMOUR-JONES METHOD.—The strength of disinfectant originally recommended by Seymour-Jones (mercuric chloride, 1 to 5,000, plus 1 per cent of formic acid) was not found to be efficient, even without neutralization of the disinfectant. A lower dilution, 1 to 2,500, plus 1 per cent. of formic acid, was found to be efficient where no neutralization was attempted. The latter strength was not sufficient, however, to prevent fatal infection of guinea pigs by disinfected material when the disinfectant was neutralized by a 1 per cent. sodium sulphide solution three or four days after the completion of the process of disinfection. No infection was caused by the inoculation of material which had been kept a week or more after disinfection. It seems, therefore, that the Seymour-Jones method might be employed with dilutions of mercuric chloride, 1 to 2,500, plus 1 per cent. of formic acid, provided the treated hides are not to be subjected within a week or two to the action of any substance which will neutralize the disinfectant. This would

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be the case, for instance, if hides were disinfected at foreign ports before shipment to this country.

(2) THE SCHATTENFROH METHOD.—Hydrochloric acid and sodium chloride in the proportions of 2 per cent. of the acid and 10 per cent. of the salt and with 48 hours' exposure have proved efficient in every instance. Consequently from the bacteriological standpoint the Schattenfroh method seems to be entirely satisfactory. This conclusion is supported not only by this work but by the exhaustive researches of Gegenbauer and Reichel[3] and Hilgermann and Marmann[4]. The recently published work of Sevcik[15] is not so favorable to the Schattenfroh method as that of the investigators previously mentioned. He finds that complete disinfection can be accomplished when the hides worked with are thin. But when the hides are thick and heavily infected, he was able, after very thorough neutralization, to extract from pieces of the treated hides anthrax spores which were virulent for mice, and in some instances for guinea pigs, even after exposure to a solution of 2 per cent. of hydrochloric acid plus 10 per cent. of sodium chloride for 7 days.

Although in view of the above-mentioned results the Schattenfroh method can not be regarded as perfect, it nevertheless seems to be far superior to other methods and well worth a trial as a standard method for the disinfection of hides.

(3) EFFECT OF DISINFECTION UPON HIDES AS REGARDS TANNING.—Mr. F. P. Veitch, Chemist in Charge of the Leather and Paper Laboratory of the Bureau of Chemistry, has been kind enough to furnish the following memorandum in regard to the tanning of small pieces of normal hide treated by the Seymour-Jones and Schattenfroh processes of disinfection.

No marked differences in color were noted among the various pieces of tanned leather. Slight differences, due to difference in thickness, were noted in pliability, but these did not appear to be connected with the disinfecting treatment. No marked difference could be detected in the appearance of the grain of the leather. All the pieces cracked when severely bent, owing probably to excessive tannin in the grain of the leathers. The treated leathers did not display more pronounced cracking than those which were not treated. Microscopical examination of the hide fibers after deliming and of the leather fibers after tanning shows no marked differences among the several pieces of hide.

The results in general seem to indicate that the several treatments have

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not injured the hides. The evidence, however, is not sufficient to permit of definite conclusions being drawn at this time. More extended work in commercial tannery, using whole hides, has been planned to determine definitely whether any of the disinfectants result in the production of inferior leather. Since tanning is a slow process, it will require from nine months to a year to secure these data.

Mr. Veitch also states that all the leathers gave reactions for chlorides, but that the leathers treated with disinfectants apparently contained larger amounts of chlorides than the other leathers.

It seems, then, so far as the evidence at hand permits any conclusion at all, that neither the Seymour-Jones method nor the Schattenfroh method exerts any injurious effect upon hides or leather.

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## NOTE ON THE SAPONIFICATION VALUE OF OILS.*

*By D. Woodroffe, M.Sc.*

In a recent report of the Oils and Fats Commission of the I. A. L. T. C. (see this J., 1915, pp. 7-18), Dr. Fahrion, as chairman, criticises other members' methods of determining the saponification value. He claims that the oil should only be boiled ten minutes with the alcoholic potash. As this seems a very short time for complete saponification experiments were made with various oils to determine this value by the two methods. About 2 grams of oil was weighed out in each case and 25 cc. of N/10 alcoholic potash was added to it in a conical flask. This was fitted with a cork and long air condenser. The flask was placed in boiling water for ten minutes and then the usual procedure was followed for determining this value by Dr. Fahrion's method.

| | Dr. Fahrion's method | | ½ hour heating | |
|---|---|---|---|---|
| Castor oil | 181.0 | 182.0 | 181.8 | 181.9 |
| Olive oil | 167.7 | 175.8 | 207.4 | 208.0 |
| Hemp seed | 186.2 | 162.6 | 193.0 | 192.5 |
| Cod oil | 175.0 | 172.0 | 176.5 | 175.5 |
| Japan fish | 179.0 | 186.3 | 183.5 | 185.0 |
| Whale | 166.5 | 139.0 | 188.3 | — |
| Walrus | 156.0 | 207.0 | 187.5 | 185.5 |
| Spanish sardine | 101.0 | 76.6 | 124.1 | 126.3 |

It is evident from these figures that 10 minutes boiling is not quite sufficient for complete saponification. Half an hour is ample time in every case even with fish oils so that it is possible that a shorter time than ½ hour would be sufficient for complete saponification of most oils met in the leather industry.

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## ABSTRACTS.

**Copper and Extraction Apparatus.** ANON. *Gerber Courier*, Jan. 8, 1916. The firm of R. Rieder & Peratoner have devised an extraction and evaporating apparatus which appears from the illustration to be made of wood. It is said to possess great advantages in the matters of space occupied and speed of operation. No complete description is given.

L. B.

* *Collegium*, London Edition, 1915, p. 336.

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**Theory of Unhairing.** ANON. *Conceria*, 23, 496. Unhairing may be accomplished through the chemical influence of alkali upon the substance of the hide or through the influence of ammonia which is developed by putrefaction. There is a difference in the water content of hides which have been subjected to these processes. Hides which have been subjected to warm putrefaction have the smaller water content. The reason for this phenomenon may be found in the van't Hoff-Arrhenius theory. In view of the relatively slight electrolytic dissociation of ammonia the difference between the osmotic pressure at the interior and exterior of the hide is small and there is consequently little flow of liquid. In the case of unhairing by liming the calcium hydroxide is a relatively strong base; the substance of the hide is readily permeable by calcium hydroxide in view of the degree of dissociation of the latter. The hide becomes greatly swollen as a result of the penetration of calcium hydroxide. If the lime liquor becomes putrid with time (and hence enriched in its content of ammonium salts and combinations of organic bases) the electrolytic dissociation of the calcium hydroxide diminishes and the osmotic pressure is consequently decreased; the swelling action of a lime liquor is, therefore, diminished by putrefaction. When sodium monosulphide is used in connection with lime the formation of sodium hydroxide must be taken into account in connection with the principles stated above.

H. S. PAINE.

**Artificial Tannin Derived from Gallic and Arsenious Acids.** ANON. *Conceria*, 22, 147. On boiling a solution of gallic and arsenious acids, Schiff obtained a product which precipitated gelatine like tannin. This compound was termed digallic acid. Subsequent experiments failed, however, to give uniform results and the product decomposed with reformation of gallic acid which had no tanning action. It is probable that the product was a definite compound of gallic and arsenious acids of slight stability. H. S. PAINE.

**Artificial Leather.** ANON. *Conceria*, 22, 98. Robe proposes the following method for preparing artificial leather. A collodion is prepared by treating cotton with 20 per cent. sulphuric acid and 9 per cent. potassium nitrate. This collodion is formed into rather thin sheets which are dried, treated in the cold with sulphuric acid, washed freely with water and finally with dilute ammonia water. Sheets of the desired thickness are then obtained by sticking these thin sheets together by means of a gelatine solution or preferably with albumen. The sheets thus prepared may be tanned with alum or tannin solution. These sheets may be colored by processes similar to those employed in the case of hides. This artificial leather is similar to genuine leather in many respects; it is, however, impermeable to air. H. S. PAINE.

**The Importance and Use of Artificial Tanning Materials.** J. PAESSLER. *Ledertechnische Rundschau*, Jan. 6, 1916. The preparation by Fischer and

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Freudenberg in 1912 of pentagalloyl glucose, a body which in most of its properties is identical with the tannin of nut-galls, while of great importance from the point of view of the scientific study of the chemical constitution of the tannins, has as yet no practical value. Stiasny followed with a discovery of great practical value, preparing bodies which, although not very near to the tannins in constitution, yet in their general properties, especially from a purely tanner's standpoint, may be said to resemble the natural tannins. From phenols, formaldehyde and sulphuric acid he prepared soluble condensation products with valuable tanning properties. Resin-like products had been made from this class of substances before, such as bakelite, all of which are insoluble and have no tanning properties. Description of the preparation of neradol D and its properties follows, all of which has been repeatedly published in this JOURNAL. The somewhat higher price of neradol in time of peace was offset by the advantages of good color, rapid working and toughness of product. The price is now higher, but it has not risen so much in proportion as that of vegetable materials, so that its extended use, especially in combination with other materials, is to be recommended in the making of many kinds of leather.

L. B.

**Contribution to the Knowledge of Chestnut Extract.** L. POLLAK. *Collegium,* 1915, pp. 435-40. The pentose content of chestnut, which the author has followed from the wood all the way through the process to the finished extract, gives valuable information in regard to the differences between many liquors in the matters of decolorization and clarification, the differences in viscosity and the variations in red figure (Lovibond), all of these being directly related to the pentose content. (See this JOURNAL, abstr. page 571, vol. 9.) The methods used in the research on pentoses will not suffice for a complete determination of lignin. For the estimation of this constituent of wood there exists an interesting scientific method by Cross, Bevans and Briggs (*Chem. Ztg.,* 1907, p. 725). This method rests on the estimation of the "phloroglucin absorption value," due to the formation of a lignin phloroglucid, without color reaction. This titrimetric estimation is, with a little practice, simple and accurate, and is more rapid than the precipitation and estimation of furfurol phloroglucid, as used in the estimation of pentoses. The method is described as follows in the original memoir:

> "Necessary solutions: (1) 2.5 grams phloroglucin in 500 cc. HCl, specific gravity 1.06; (2) 2 grams furfurol in 500 cc. HCl, specific gravity 1.06, *or* 2 cc. formaldehyde, 40 per cent. in 500 cc. HCl, specific gravity 1.06.
>
> "Digestion: Two grams finely divided wood are dried at 100° C. and weighed; then transferred to a dry flask and covered with 40 cc. phloroglucin solution. The flask is corked, shaken and let stand a few hours, best over night. In the morning the liquid is filtered off through a very small cotton plug in the neck of a funnel, and 10 cc. measured out with a pipette into a titration flask.

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"Titration: The 10 cc. are diluted with 20 cc. of HCl of specific gravity 1.06 and heated to about 70° C. The furfurol or formaldehyde solution is then added from a burette in quantities of 1 cc. at a time. After each addition of 1 cc. the liquid is allowed to stand for 2 minutes before testing, at a constant temperature of 70° C. The progress of the reaction is followed by placing a drop of the liquid without filtration on the indicator paper, which is partly sized cheap printing paper. The drop is allowed to stand for 10 seconds and then shaken off. A red spot will then be visible so long as any unprecipitated phloroglucin is present. Near the end of the titration, the solution should be added in 0.25 cc. portions, waiting as before 2 minutes before making the test. Near the end-point, the red spot appears more and more slowly, and at last the damp place must be dried by holding it 20 cm. above the flame of a Bunsen burner in order to observe the spot. The titration is finished when no red spot can longer be seen.

"After the titration, 10 cc. of the original phloroglucin solution are titrated as a control in exactly the same manner, and the quantity of phloroglucin absorbed by the ligno-cellulose is calculated from the difference between the two titrations. This phloroglucin absorption is then expressed as a percentage of the dry weight of the ligno-cellulose."

This fully worked out method for wood the author sought to extend to extracts, and used the following procedure. From 1.5 to 3 grams of extract, according to the concentration, were evaporated to dryness three times on sand, and then dried 2 hours at 100° C., cooled, covered with 40 cc. phloroglucin solution, thoroughly shaken several times and let stand covered over night. The liquid is poured off into a wine glass and set aside for a longer or shorter time, depending on the kind of extract, finally the clear liquid is poured through a small filter with a cotton plug; 10 cc. of the liquid are then titrated as above. The simple shaking of the extract with phloroglucin without previous drying was tried, the results calculated in both cases as percentages of the dry residue. Four samples of chestnut extract gave the following results by the drying process: 4.17, 4.40, 5.66, 5.01. By the wet process the same samples gave the following, respectively: 8.20, 10.54, 9.58, 7.81. This difference is due to the presence in the extract of aldehydes, especially furfurol, which form phloroglucids, and so consume some of the phloroglucin. The drying process expels these aldehydes, since they are volatile bodies. Four samples of chestnut wood gave the following phloroglucin absorption values: 4.40, 4.56, 4.21, 4.11. The spent wood from the same woods gave the following respective values: 4.49, 4.41, 4.44, 4.41. The extraction took place in copper batteries under pressure. The differences between these values for new and spent wood are inconsiderable, from which it may be concluded that no solution of the lignin of the wood has taken place in the process of extraction. This, however, is not the case, for, as may be

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seen from the figures above, the extract gives a large figure for phloroglucin absorption. Reckoned on the tannin, this figure for the wood is 32 per cent., and for the extract, 16 per cent. This is due to the continual formation from the lignin-complex of new quantities of lignin substance which absorbs phloroglucin. According to Cross and Bevan, the absorption of phloroglucin is due to the "ketocyclohex" or chinoid group of the lignin complex. It must therefore happen that during the extraction of the wood ketocyclohex is continually being formed out of the non-cellulose (lignin residue), which Cross and Bevan briefly denote as "lignon," and that the ketocyclohex goes partially into solution. This process is always combined with a simultaneous formation of pentoses, formed from the residue of the lignon. It appears, however, that in different chestnut woods the ketocyclohex is combined with varying amounts of pentoses. This question cannot as yet be answered with certainty.

Comparison of chestnut and quebracho wood is of great interest. More non-tans are formed in the extraction of chestnut wood than in the case of quebracho. Most of those experienced in extraction explain the appearance of larger quantities of non-tans as a result of the decomposition of tannin by heat and pressure. The author concludes that, at least in most cases, the destruction of tannin is practically nothing, but that nearly all the non-tannin arises from the decomposition of the wood. For quebracho the following phloroglucin absorption values were obtained: wood, 1.42; Triumph liquid extract, 0. Estimation of the "raw fiber" according to König gave 46.16 per cent., of which 27.99 per cent. was cellulose and 18.17 per cent. lignin. The percentage of pentoses in the wood was 11.54. The lignin figure (König) is two or three times that of chestnut wood, while the phloroglucin absorption figure is only one-third as much, showing that the two methods of estimating lignin do not agree. The pentose figure for quebracho, as was to be expected, is notably lower. We may conclude that a wood with small phloroglucin absorption and little pentose content resists the decomposing effect of extraction better than a wood with higher figures. In the following table the four samples of chestnut wood mentioned above are compared with the sample of quebracho.

| | I | II | III | IV | Quebr. |
|---|---|---|---|---|---|
| Tannin | 12.50 | 13.50 | 13.20 | 13.20 | 19.00 |
| Non-tannins | 2.20 | 1.30 | 2.20 | 1.90 | 1.90 |
| Cellulose | 27.07 | 29.95 | 27.32 | 27.05 | 27.99 |
| Lignin (König) | 10.83 | 7.10 | 6.64 | 6.72 | 18.17 |
| Phloroglucin absorption value | 4.40 | 4.56 | 4.21 | 4.11 | 1.42 |
| Pentoses | 19.06 | 18.87 | 18.32 | 15.28 | 11.54 |

Hope was entertained that the phloroglucin absorption number might afford a means of identifying different extracts, especially of detecting the presence of sulphite-cellulose extract, since it might with reason be expected that sulphite-cellulose extracts would give high values. This hope has not been realized, as the following figures show. Values for



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extracts not previously mentioned are: for three oak wood extracts (all figures percentages of dry residue), 4.45, 4.29, 4.86; solid quebracho, 1.32; sulphited quebracho, 0.18, 0.0; sulphite-cellulose extract, 7.88, 4.40, 4.53, 4.07. Only adulteration of quebracho could be recognized with any certainty. L. B.

**China's Leather Imports.** Vice Consul G. J. BARRETT, Shanghai. *Commerce Reports.* The importation of leather and leather manufactures into China has steadily increased in recent years. Among the reasons for this were the purchases of new equipment for China's army, including boots, shoes, belts, etc.; the establishment of cotton, silk, and flour mills, which has created a demand for belting; and the adoption of the Western style of dress by many of the Chinese, with incidental purchases of shoes, trunks, bags and other articles. Although a few tanneries have been established in the coast and principal cities, and, to some extent, in the interior (one of some importance in Szechwan Province), they have not been, thus far, very successfully operated. Various causes are responsible for this condition, poor business management and a lack of proper technical knowledge of the trade being predominant. There are indications that China will continue to have a great part of its leather needs supplied from abroad for some time. The net imports of leather and leather manufactures into China for the last four years have amounted to from $3,000,000 to $5,000,000 annually. Much of this traffic is trans-shipped at Hong Kong, so that it is not possible to trace the origin from the Chinese customs reports. Of leather manufactures, approximately 50 per cent. come from Japan. The advantages possessed by Japan due to nearness, low cost of production and possibility of prompt delivery give to that country a practical monopoly in low-priced goods. The importation of boots and shoes in 1914 amounted to 227,000 pairs, valued at about $393,000. Three tanneries are located at Shanghai. They have been operating with but moderate success. The principal one is controlled and operated under foreign supervision, the others are managed and capitalized by Chinese and Japanese, respectively. The manager of the foreign-controlled tannery frankly admits that it has not had a successful year, chiefly on account of the difficulty of obtaining coloring extracts, which heretofore had been mostly supplied from France and Italy. There is but little demand for harness leather. This was supplied before the war largely by Great Britain, most of it coming from England. The approximate price at that time was $0.48, United States currency, per pound. To-day the price is about $0.83 per pound. It is claimed that American harness leather is not suitable for use here, being too hard. A small demand for trunk leather exists. This, however, is supplied chiefly by the Japanese. Some years ago American leather was largely shipped into China, but the Japanese gradually displaced it to a large extent, though it is claimed that a fair percentage of the leather which Japan sends here was originally exported from the United States. This particularly applies to leather of superior quality.

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**Osage Orange Competes with Fustic.** *Commerce Reports*, Feb. 3, 1916. The production of osage orange extract on a commercial scale has been established, and this material is now available for the tanning, textile, paper, and other industries, wherever a natural dye can be used. It is hoped that this will serve not only to relieve the situation caused by a shortage of aniline colors in certain shades, but also in normal times to replace the use of foreign fustic by a wood indigenous to our own country. The study of osage orange as a dyewood was begun by the United States Forest Service about three and one-half years ago, and was the result of an investigation of the utilization of osage orange mill waste. As about 4,000 tons of fustic were imported annually for dyes, a series of competitive dyeing tests was made between the extract obtained from osage orange and that from fustic. This work was then extended by the co-operation of a number of textile schools. Later the material was tried out as a leather dye by Dr. L. E. Levi, of Milwaukee, and the entire subject was brought before the American Leather Chemists' Association last May, at the Atlantic City meeting. A prominent firm became interested in the subject at this time and is now producing the extract on a commercial scale. The dye is the same as that present in fustic, but it is a pure compound, free from the varying admixture of a reddish coloring matter, which renders the use of tropical fustic somewhat uncertain. The orange-yellows, old gold, deep tan, olive, and chocolate chades obtained with chromium and iron mordants are equal to, if not better than, those obtained with the use of fustic. The mill waste alone from the present manufacture of osage orange amounts to more than 25,000 tons annually, and if this waste could be set down at the mill for $10 to $12 per ton, it is believed that it could compete successfully with fustic in both cost of production and quantity of color produced. The osage orange is found in large quantities in the Mississippi Valley and is especially abundant in Oklahoma and Texas.

**Analysis of Dutch, English and American Sole Leather.** *Hide and Leather,* Dec. 25, 1915. *De Nederlandsche Lederindustrie* publishes an interesting article regarding comparative analysis of American, Dutch and English sole leather. Neither in Holland, nor in the United States nor England, will tanners be found who tan sole leather with pure oak bark exclusively. Modern tanning requires quicker methods. The use of extracts brought an entire change in the sole leather manufacture. The result of this new invention was the drum tannage. The quality of sole leather was not improved by this new tanning method. Many shoes manufacturers deplore the disappearance of the real good and old-fashioned oak-tanned sole leather. Oak-tanned sole leather contains only 8 to 10 per cent. of water soluble materials. With the mixed tanning method this percentage is much higher. A sample of Dutch sole leather, mixed tannage, contained about 16 per cent. of soluble materials. In pure extract tannage this percentage is still higher. Experiments by the Government experimenting station at Waalwyk, Holland, show that the average per-

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centage of soluble materials present in Dutch extract-tanned sole leather is 18.6. However, among the samples sent in for examination there were some which contained as much as 26 and 27 per cent. of soluble materials. The English Federation of Tanners recently decided that 25 per cent. should be taken in England as a limit. The following figures show the results of thirty-two analyses of Dutch sole leather taken recently at the experimenting station at Waalwyk, Holland:

DUTCH SOLE LEATHER.

| | Per cent. |
|---|---|
| Moisture | 19.4 |
| Ash | 0.6 |
| Soluble organic materials | 11.3 |
| Hide substance | 41.2 |
| Combined tanning materials (tannin) | 27.1 |
| Sugar containing materials | 0.6 |

The analysis of three samples of English leather gave the following results:

ENGLISH LEATHER.

| | A. Per cent. | O. Per cent. | S. Per cent. |
|---|---|---|---|
| Hide substance | 36.63 | 36.32 | 37.10 |
| Soluble organic materials | 31.40 | 32.00 | 21.10 |
| Soluble ash | 0.72 | traces | traces |
| Insoluble ash | 0.50 | 0.58 | 0.60 |
| Combined tannin | 19.37 | 17.00 | 25.20 |
| Moisture | 12.10 | 14.10 | 16.00 |
| Sugar containing materials | 2.25 | traces | traces |
| Epsom salt | traces | 1.6 | traces |

Sample S is of good English tannage; samples A and O are of leather of the quick tanning method, such as is the actual system in England. They represent the leather as now made, and, of course, cannot be called "standard" tannage, because it has been tanned quickly to satisfy the urgent demand. Analyses of English leather tanned before the war do not show the high percentage of soluble organic materials. Most of them contain about 23 per cent. Only a few showed a trifle over 25 per cent., but none contained over 30 per cent. The analysis of four samples of American sole leather showed the following results:

AMERICAN SOLE LEATHER.

| | B. Per cent. | C. Per cent. | D. Per cent. | E. Per cent. |
|---|---|---|---|---|
| Hide substance | 35.52 | 36.63 | 32.07 | 38.23 |
| Soluble organic materials | 31.20 | 22.10 | 26.90 | 22.00 |
| Soluble ash | 1.80 | 0.20 | 1.84 | traces |
| Insoluble ash | 0.90 | 0.36 | 0.60 | 0.68 |
| Combined tannin | 18.66 | 28.65 | 28.21 | 26.31 |
| Moisture | 13.72 | 12.26 | 12.22 | 12.78 |
| Sugar containing materials | 9.76 | 3.42 | 5.34 | traces |
| Epsom salt | 4.85 | traces | 4.53 | —— |

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Two other samples of American sole leather recently imported showed the following analysis:

| | F. Per cent. | G. Per cent |
|---|---|---|
| Ash | 0.8 | 2.0 |
| Epsom salt | none | 3.4 |
| Soluble organic materials | 17.3 | 25.8 |
| Sugar | 2.5 | 7.9 |

As to the origin of the samples of American leather, sample B was of sole leather of a large corporation and so-called "scoured bends." Sample C are "unscoured bends" of the same tanners. Sample D is of butts made by another leading American tannery corporation, whereas sample E is a very good oak bark tanned product of Kentucky. Evidently this leather has been tanned by the old system, and we guess that the tannage has lasted about one year. The American sample E is the best by far. The price is said to be 59 cents a pound, which is cheap enough for such a good product. It is a remarkable fact that the average percentage of soluble organic materials in the Dutch leather is 11.3, while sample E of the American sole leather shows 22 per cent. The ash percentage is the same and also the hide substance. However, the percentage of moisture with the Dutch leather is 19.4 per cent., while the American leather contains only 12.78 per cent. This is a very important difference. Of the other samples of American leather, C and F are the best. Still both contain 3.42 and 2.5 per cent. sugar, whereas the allowed sugar percentage is only 2 per cent. Epsom salt was absent. The ash percentage is normal and the percentage of organic soluble materials is also as it ought to be.

For sample B 59 cents was paid, whereas leather of sample C brought 55 cents a pound. So double was paid for the glucose and the Epsom salt, for there is no worse sample than the scoured oak bends of sample B. A high percentage of soluble organic materials, a high ash percentage and besides 9.76 per cent. of sugar and 4.85 per cent. of Epsom salt were shown in the analysis. This analysis teaches us that it is almost impossible to judge American leather by its looks, because the leather of sample B looked all right on the grain. It was higher priced than the other sorts, but still the unscoured bends proved to be of far superior quality.

Sample D is leather tanned by a leading sole leather producer, is hemlock tanned and costs 49 cents a pound. The soluble organic materials are not so strongly represented as in sample B (26.9 per cent. against 31.2 per cent.). The ash percentage is 2.4 per cent. against 2.7 per cent. in B. Also glucose and Epsom salt are present, but not to such great extent as in B. It is a remarkable feature that B shows such a small percentage of combined tannin, which certainly indicates quick tannage and the use of tanning materials of great strength. Most probably

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mechanical means have been used to work the extract into the leather. Sample D also contains a large percentage of glucose and Epsom salt, but still the tanning of that leather is far superior to that of B.

## PATENTS.

**Leather Splitting Machine. U. S. Patent 1,164,829.** H. LYON, Brockton, Mass., Assignor to Thomas Bostock and Sons.

**Waterproofing Leather. U. S. Patents 1,166,845 and 1,166,846.** ROBERT A. MARR, Norfolk, Va. Leather is immersed in a melted mixture of resin and paraffine with diatomaceous earth at the boiling point. In the second patent, naphthalene is substituted for resin.

**Flexible Waterproof Leather. U. S. Patent 1,167,326.** J.W. BARBER, Newton, Mass. The materials are paraffine and petrolatum.

**Process of Tanning. U. S. Patent 1,167,951.** J. G. STODOLA, Assignor to G. J. A. Trostel, Milwaukee, Wis. The process involves first pickling, then giving a preliminary chrome tannage, then placing the hides in a solution containing both basic iron compounds and basic chromium compounds.

**Leather Stretcher Dropping Device. U. S. Patent 1,169,974.** C. B. LEONARD, Philadelphia, Pa.

**Preparing Hides and Skins for Tanning. U. S. Patent 1,170,426.** E. D'HUART, Luxemberg. The process consists in treating the skins with a bate made up of glycerophosphoric acid and one of its salts.

**Sulphonated Hydrogenized Oils. British Patent 16,889.** I. LEVINSTHIN, Manchester.

**Sulphite-Cellulose Extracts. British Patent 18,332.** W. E. HORROCKS, Knutsford, Cheshire.

**Solubilizing Reds in Quebracho. British Patent 17,273.** H. FRANKE, Wilsdorf. The hot liquor is treated with lime afterward neutralized with acid.

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## COUNCIL MEETING.

A meeting of the Council was held at the Chemists' Club, 50 E. 41st St., New York, on February 26, 1916. Messrs. Haley, Teas, Small, Faust and Reed were present.

It was decided to hold the next annual meeting at Atlantic City

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on June 1, 2 and 3, 1916. The Secretary was deputed to ask the hotels for rates and submit data to the Council.

Mr. C. C. Smott, III, was appointed Chairman of the Committee on the Cure and Disinfection of Hides in place of J. H. Yocum resigned, and Cudworth Beye was added to the Committee.

The Committee on Uniform Blanks for Tannin Analysis, E. J. Haley, Chairman, was requested to submit forms for the vote of the active members of the Association.

Mr. F. H. Small was appointed to draft suitable resolutions in regard to the death of C. W. Norris.

Frank S. Hunt and R. L. Schell were elected to associate membership.

Nominations were made for the forthcoming election of officers.

A suggestion in writing from A. C. Orthmann that discussion at annual meetings be limited to papers already published in the JOURNAL was discussed, but not approved.

As Committee on Program, Messrs. Walling, Beye, Morrison, Teas, Levi and Veitch were appointed.

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## A SIMPLE VACUUM DISTILLING APPARATUS.

*By T. G. Greaves.*

A vacuum distilling apparatus is frequently used in laboratories for concentrating liquids or distilling at as low a temperature or as rapidly as possible. It was recently found to be difficult to replace parts or get a new unit because of war conditions, so a simpler form was devised, which is also more satisfactory, because it eliminates a joint with a rubber ring which experience has shown is liable to leak and affect the reduction of pressure.

The apparatus listed in the catalogues at $7.00 to $7.50, without thermometer or water bath, consists of a heavy, flat porcelain dish made to fit into a pan (water bath) and a glass dome which rests on a rubber ring which is the packing of the joint between the dish and the dome. The top of the dome has a ground opening into which fits a tube which has a side branch to convey

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vapor to the condenser and the top of which has a rubber stopper with a hole for a thermometer.

In place of this we are now using a glass gallon whiskey jug, which costs 10 cents, with a rubber stopper carrying a bent tube to convey vapor to the condenser and a smaller hole which can be used for a thermometer. A thermometer is not used, however, as the vacuum gauge gives the approximate temperature, but in place of it a bent tube which connects by a rubber tube with a supply of the liquor so that the apparatus may be refilled by opening a pinch cock, without breaking the vacuum. The jug is placed in a sauce pan of water with pieces of metal or glass tubing in the bottom to keep it from being cracked by boiling the water. The diameter of the jug is the same as that of the German apparatus. It holds the maximum vacuum uniformly without watching. It can be adjusted so that the liquid drips into it constantly.

Laboratory of John H. Heald & Co., Inc.,
Lynchburg, Va.

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## THE ACTION OF SALTS OF HYDROXY-ACIDS UPON CHROME TANNING.*

*By Henry Richardson Procter, D. Sc., and John Arthur Wilson.*

(Contribution from the Procter International Research Laboratory.)

[EDITOR'S NOTE.—The international character of the Research Laboratory is illustrated by the fact that Mr. Wilson is an American. His contributions to the JOURNAL in 1913 and 1914 (in collaboration with Douglas McCandlish) were from Milwaukee.]

The theory of chrome tanning assumes that tanning will take place if the basicity and concentration of the chromium salt are properly regulated. But cases have arisen where skins would not tan in certain liquors, even when these liquors were rendered very basic. An investigation has revealed the interesting fact that the presence of salts of many, if not all, of the hydroxy-acids has a very marked influence upon the tanning power of chromium salts.

* *J. S. C. I.* Feb. 15, 1916, pp. 156-9.

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The first salt experimented upon was potassium sodium tartrate, ordinarily known as Rochelle salt. It was found that if much of this salt be added to a chrome liquor, the latter is rendered incapable of tanning. Such a liquor gives no precipitate when rendered slightly alkaline with sodium carbonate. Immediately after Rochelle salt has been added to a chrome liquor the latter may give a precipitate if rendered alkaline, but the precipitate will slowly re-dissolve. If the mixture of salt and chrome is allowed to stand for several hours before adding the soda, no precipitate is formed. It was noted further than an addition of Rochelle salt to a solution of chrome alum produces a change of color.

These preliminary experiments recall the fact that in qualitative analysis the presence of hydroxy-compounds prevents the precipitation of the metals as hydroxides. The metal ion enters, in the negative ion of such hydroxy-compounds as tartrates and citrates. The action is reversible, but the complex ion formed is very slightly ionized, and furnishes even less of the metal ion in solution than does the nearly insoluble metallic hydroxide. This accounts for the fact that Rochelle salt re-dissolves a precipitate of chromium hydroxide.

A chrome liquor was prepared from chrome alum by treating with sodium carbonate in the usual way. From this a series of eight solutions was prepared, varying in concentration of Rochelle salt as follows:

| Solution No. | Grms. chrome oxid per liter. | Grms Rochelle salt per lite |
|---|---|---|
| 1 | 13 | 50 |
| 2 | 13 | 25 |
| 3 | 13 | 10 |
| 4 | 13 | 5 |
| 5 | 13 | 2.5 |
| 6 | 13 | 1 |
| 7 | 13 | 0.5 |
| 8 | 13 | none |

Temperature 24° C.

Into each liquor was put a piece of calfskin which was in a practically neutral condition. The liquors were agitated occasionally, and at the end of 24 hours the skins were examined. That in No. 1 was of a bluish color, while that in No. 8 was rather a green, the others varying in shade from blue to green. The skin in No. 1 was unusually full and soft, this property becoming less

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and less marked in the others down to No. 8. But all the skins were nearly or quite tanned, excepting those in Nos. 1 and 2.

Upon adding 150 cc. per liter of N/1 sodium carbonate solution to each liquor, heavy precipitates formed in all but Nos. 1 and 2. In No. 2 there was a lighter precipitate, but in No. 1 there was none. Four hours later the skin in No. 2 was tanned, but that in No. 1 was still untanned. We added 300 cc. per liter of N/1 sodium carbonate, in two portions, to No. 1, and still no precipitate formed, although the liquor was now alkaline to phenolphthalein. Forty-eight hours later the skin was still not tanned.

To make certain that the action of the Rochelle salt was upon the chrome rather than upon the skin, we immersed a piece of skin in a solution of N/1 Rochelle salt for several hours, allowed it to drain, and then put it into a large volume of fresh chrome liquor. The volume of liquor was taken so large that, when the Rochelle salt diffused, its concentration would not be sufficient to prevent tanning. The skin tanned very well.

The piece of skin from No. 1, which had not tanned, was now washed, to free it from salt, and placed in a fresh chrome liquor. In a few hours it was completely tanned.

All of the above experiments were repeated with neutral sodium citrate, using equivalent concentrations. The results were apparently identical with those obtained with Rochelle salt. It was also found that the sodium salts of lactic, gallic, and salicyclic acids prevent the precipitation of chromium in slightly alkaline solutions.

As to possible sources of these compounds in chrome liquors, it is conceivable that they might be formed in quantities sufficient to prevent tanning by reducing the bichromate with impure sugars or by reducing under improper conditions. Sugars themselves are hydroxy-compounds, and very probably yield an abundance of hydroxy-compounds of smaller molecular weights when the oxidation is very incomplete or is carried on at too low a temperature, and it is known that under certain conditions mucic and saccharic acids are formed by the oxidation of carbohydrates. An experiment was tried reducing bichromate at as low a temperature as possible with a commercial dextrine. The result was

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a liquor which did not at once give a precipitate upon rendering slightly alkaline and became turbid only on long standing. A piece of skin immersed in it tanned with difficulty, and only after adding an excess of sodium bicarbonate. In color and feel the leather resembled that from No. 2 in the experiments with Rochelle salt.

To deal with the very complex nature of the formation of hydroxy-compounds from the incomplete oxidation of the sugars is beyond the scope of our present research. We shall not even attempt an explanation of the exact reason why the chrome liquor in question behaved as it did. It is sufficient for our purpose to state that, in order to insure the production of a satisfactory chrome liquor by reducing bichromate with sugars, it is necessary to use reasonably pure sugar, and conditions found to produce a satisfactory liquor should be closely adhered to.

Since sugars themselves are hydroxy-compounds, it might seem that an excess of sugar in a chrome liquor would prevent tanning. As a matter of fact, an excess of sugar, although it produces the fulness characteristic of the effect produced by Rochelle salt, does not prevent tanning, even when present to the extent of 20 per cent. An explanation of why sugars do not prevent tanning is offered by a consideration of the action of Rochelle salt in forming metallic complexes. Rochelle salt has the formula,

$$KO.CO.CH(OH).CH(OH).CO.ONa.$$

This salt ionizes not only into sodium, potassium and tartrate ions, but the tartranion ionizes slightly to a still further extent by giving off hydrogen ions from the hydroxyl groups. Since the sodium salt formed by replacing the hydrogen of the hydroxyl groups by sodium is readily ionizable, the addition of sodium hydroxide to a solution of Rochelle salt will result in the neutralization of the hydrogen ions, and a consequent increase in concentration of the tetravalent negative ion. But this negative ion forms with the heavy metal salts which are very slightly ionized. The most familiar example of this is found in Fehling's solution. When copper sulphate is added to an alkaline solution of Rochelle salt a slightly ionizable cupri-tartrate-ion is formed,

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$$\begin{array}{c} O.Cu.O \\ | \quad | \\ -O.CO.CH-CH.CO.O- \end{array}.$$

It is evident from the foregoing that, if the hydroxyl groups of a certain compound readily give off hydrogen ions, and if the resulting negative ion forms a very slightly ionizable salt with the heavy metals, no addition of alkali will be necessary to form the metallic complexes. But, if the hydroxyl groups do not ionize sufficiently readily an addition of alkali will be required to bring the concentration of the negative ion up to the point required to combine with the metal ion.

This is evidently the case with sugar. If the salt of a heavy metal is added to a solution of sugar, a considerable excess of alkali is required to form the complex. On the other hand, Rochelle salt forms the complex with chromium without addition of alkali.

The formation of the metallic complexes with hydrogen-compounds is discussed somewhat in detail because of its bearing upon points to be discussed presently.

It was originally intended that this research should consist only of a few simple experiments to determine possible reasons why certain chrome liquors refused to tan. But it soon became evident that the subject is rich in possibilities both for theoretical and practical work. Many ideas for the practical application of the principles discussed presented themselves. Of these we shall mention the most promising, leaving it to those to whom any point appeals directly to carry on the research in greater detail.

Probably the most important property of Rochelle salt in this connection in its power to strip chrome leather of its chromium. This property was suspected from the fact that the salt will redissolve precipitates of chromium hydroxide. A piece of chrome leather was immersed in a normal solution of Rochelle salt over night. Upon subjecting to the boiling test, it was found to be no longer tanned. It was then washed and immersed in a fresh chrome liquor. It was again soon fully tanned, showing that chrome tanning is a reversible process.

Experiments were then tried to see how completely it was possible to strip the leather. A piece of air-dried chrome calf was immersed in a cold, normal solution of Rochelle salt and

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allowed to stand for two weeks. The liquor was colored a deep green. Upon being washed the skin resembled a bated calfskin, and was found to contain no appreciable amount of chrome. In this case the slow action was due to the low temperature of the liquor. A piece of chrome calf placed in such a liquor at 100° C. soon shrinks to a gummy mass.

There is a point which has long been a puzzle to many tanners. A hide is much easier to split after it has been chromed than in the raw state. But these tanners have not found nearly such a demand for chrome splits as for splits tanned with such materials as quabracho and mimosa bark. It might prove valuable to give the hides a light tannage with chrome, then split, and then strip the splits of their chrome by immersion in Rochelle salt solution. After washing they should be in a condition favorable for tanning with quebracho or mimosa bark.

Since hydroxy-compounds form complexes with other metals, including iron, Rochelle salt might conceivably be used for removing or preventing so-called salt stains. A stain produced by iron and sulphide was easily removed in this way. Treatment with Rochelle salt before liming might prove of advantage in some cases to prevent the formation of iron stains. The skins are easily washed free from the salt.

It is possible that a bath in Rochelle salt solution previous to tanning might be preferable to pickling for some kinds of leather. In the case of heavy leathers this possibly would result in a lighter, but more uniform, preliminary tannage. Such leather should be capable of taking up a much larger proportion of chromium upon being retanned in a fresh liquor, because of the even distribution of the chrome in the preliminary tannage.

While the presence of a large amount of hydroxy-compounds will prevent tanning, a small quantity does not, but does produce a fulness and softness in the leather not otherwise obtained. Many tanners have found than an excess of glucose in their liquors is desirable. Probably small amounts of Rochelle salt would produce the desired effect. The point is at least worthy of consideration.

Another use of this salt lies in its power to strip chrome leather which has been case-hardened. If very basic chrome

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liquors are used in tanning there is danger of the interior of the skin absorbing acid while the chrome is being precipitated or fixed upon the surface. The surface becomes heavily tanned while the interior is still in a raw, acid condition. A very long time is required for such a condition to right itself, but the trouble could be overcome easily enough by stripping with Rochelle salt, washing, and retanning in a fresh liquor.

And finally, this stripping power of hydroxy-compounds can be applied to the conversion of chrome shavings and cuttings into glue stock. Pieces of air-dried chrome leather were stripped of their chrome and then converted into glue and gelatine in the usual manner. The importance of this fact needs no emphasis; it is obvious.

In all of the points discussed the theory of the formation of these complexes should be constantly borne in mind. It will then be evident that, in stripping, the solution must not contain any strong acid. The presence of acid would repress the ionization of the hydroxyl groups (in which hydrion is liberated) to such an extent as to make the formation of these metallic complexes impossible. In fact, the addition of strong acid to one of these complexes will decompose it; the action being reversible. An alkaline solution is most favorable to the formation of these complexes, and where the presence of alkali will do no harm its presence will greatly accelerate the rate of action.

Since the property of Rochelle salt which has just been discussed is common, in a greater or lesser degree, to all hydroxy-compounds, the tanner has a wide choice in selecting substances most suitable for his purposes. Rochelle salt might prove too expensive to use freely as a stripping agent, but its use might be made practicable if the salt and chrome could readily be recovered. It is found that this can to a large extent be effected by the addition of sulphuric acid to neutralize the equivalent of soda and reconstitute the acid potassium salt, which is very little soluble and rapidly crystallizes out, so that it can be separated and used again with a suitable addition of soda, while the chrome can be precipitated from the mother-liquor as chromium hydroxide. Crude acid potassium tartrate ("tartar") dissolved with addition of soda would be the cheapest source of Rochelle salt. A mixture

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of equivalent quantities of lactic acid and sodium carbonate might serve his purposes just as well and would probably be a little cheaper. The practical applications of the principles discussed are problems for the tannery chemist, who, it is hoped, will find this work of value. It is also possible that uses may be found in other industries, as, for instance, in the stripping of chrome-mordanted wool.

DISCUSSION.

Mr. J. T. Wood said that the paper contained a number of very valuable suggestions. The remarks upon the removal of salt stains were very interesting and ought to be followed up, because those stains were the cause of great loss, especially in France. The suggestion about splitting and stripping the split was also very good. The Austrians and the Germans were the first to introduce splitting of kips, and in that way they had secured practically the whole trade. Now there were large quantities of them about, and nobody, except the Germans, were prepared to use them. Mr. Trotman had invented a process for stripping chrome leather, in which sodium peroxide was used; in that case he took it that the skin would not be of much use afterwards. The process was used for stripping chrome shavings, and a great quantity had been so treated by the process.

Mr. R. F. Innes said that the recovery of chrome, and also of Rochelle salt, was an important point. Recovery was always difficult in the case of liquors. In his own business hundreds of tons of chrome was allowed to run to waste. That was going on throughout the world, and no attempts seem to be made to recover such a waste.

Mr. J. M. Wilkie said his own view was that an increased demand for tartaric acid seemed to be out of the question. They were dependent upon the wine industry for tartrates, and the tendency now seemed to be to decrease production of wine. In ordinary circumstances there was great difficulty in getting sufficient tartrates for ordinary demands. He wondered whether it would not be better to use some other hydroxy acid.

Mr. Wood: English lactic acid is not so strong as either American or German.

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PROFESSOR PROCTER: Lactic acid is not a very dear acid in the crude form in which it is used in tanning.

Replying to the Chairman, Mr. Wilson said that there were a great many other sources from which hydroxy-compounds could be obtained. For instance, saccharic acid might be obtained from the decomposition of sugar.

Professor Procter, in reply, said that they had not considered the practical aspects of the problem as to cost. The investigation was suggested by the fact that certain samples of glucose, and especially white glucose, and glucose syrup, yielded liquors which were dull violet instead of blue-green, and which absolutely would not tan. Under proper control this tendency might be used to get such results as were required. He did not think it was necessary to reject chrome liquors to the extent which was commonly done, and one of his earliest efforts in tanning analysis was to invent control methods through which liquors could be strengthened for re-employment. A very small quantity of Rochelle salt would give a fuller feel; it made a thicker leather, and if tanning could be continued, a thicker and plumper leather altogether, well adapted to market requirements, would be produced. Sugar had some effect, but it was not so powerful as Rochelle salt.

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## THE USE OF NICKEL HYDROXIDE IN TANNIN ESTIMATION.*

*By Puran Singh and T. P. Ghose, B.Sc.,*
*Forest Research Institute, Dehra Dun, India.*

As shown in a paper on this subject by one of us (*J. S. C. I.*, 1911, 30, pp. 936-937), freshly precipitated nickel hydroxide serves as an excellent substitute for hide powder in the estimation of tannin. Situated as we are in India, our supplies of standard hide powder at times run short, and a reliable substitute for hide powder is a great desideratum. With this object in view, we have continued our experiments on the use of nickel hydroxide as a substitute.

Dr. H. H. Mann, of the Poona Agricultural College, was kind enough to compare the nickel hydroxide method with the copper

* *J. S. C. I.*, February 15, 1916; pp 59-60.

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acetate method, which he has been using for years in tannin estimation, and with the hide powder method, with the results shown in Table I.

TABLE I.

| | Babul pods (Pods of *Acacia arabica*). | Tarwar (*Cassia auriculata* whole plant). |
|---|---|---|
| | Tannin % | Tannin % |
| Nickel hydroxide paste method | 26.3 | 0.7 |
| Hide powder method | 23.7 | 0.84 |
| Copper acetate method | 26.6 | 0.60 |

A practical difficulty, however, confronted us in the preparation of pure nickel hydroxide free from sulphate. In the form of freshly precipitated paste, we found it extremely difficult to wash it free from sulphate except in very small quantities. The word "paste" carried no definite idea of the percentage content of nickel hydroxide contained in it. For these reasons, we had eventually to abandon the use of paste and to use the fine powder of nickel hydroxide instead. For the purpose, we obtained Kahlbaum's extra pure nickel hydroxide, which, to our great surprise, contained traces of sulphate. After repeated washing with hot water and finally with water containing traces of tannic acid, we got it free from sulphate and in a fairly granular condition. This nickel hydroxide has been used in the experiments described in this paper.

TABLE II.

| Serial No. | Description | Quantity contained in 500 cc. grms. | Quantity absorbed by nickel hydroxide powder. grms. | Quantity absorbed by chromed hide powder. grms. |
|---|---|---|---|---|
| 1 | Tannic acid | 4.56 | 4.26 | 4.41 |
| 2 | Gallic acid | 4.52 | 3.92 | 3.12 |
| 3 | Glucose | 4.76 | 2.06 | 2.36 |
| 4 | Cane-sugar | 4.94 | 2.79 | 2.39 |
| 5 | Tannic acid and gallic acid | 2.28<br>2.26 | 3.90 | 3.00 |
| 6 | Tannic acid and glucose | 2.28<br>2.38 | 2.55 | 2.26 |
| 7 | Tannic acid and cane-sugar | 2.28<br>2.45 | 2.43 | 2.48 |

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It has already been shown that nickel hydroxide forms definite chemical salts with tannic acid (*J. S. C. I.*, 1914, 33, pp. 172-173, this JOUR., 1914, pp. 186-8). It also forms an insoluble salt with gallic acid. The solutions of tannic acid, gallic acid, glucose, and cane-sugar of known strength were treated, with chromed hide powder and nickel hydroxide under similar conditions, with the results shown in Table II.

These tests gave sufficiently encouraging results to make comparative estimations with a number of tanning materials, the results of which are shown in Table III.

TABLE III.

| Description of material | Moisture | Tannin by nickel hydroxide | Tannin by hide powder |
|---|---|---|---|
| | per cent. | per cent. | per cent. |
| Mangrove bark | 12.02 | 33.95 | 35.20 |
| Mangrove extract | 14.33 | 73.13 | 76.54 |
| Sal (*Shorea robusta*) bark | 10.19 | 19.59 | 18.67 |
| Sal extract | 16.09 | 62.57 | 63.25 |
| *Cassia auriculata* bark | 9.89 | 23.42 | 21.44 |
| *Cassia auriculata* bark | — | 23.23 | 21.81 |
| Myrobalans, pulp | 14.98 | 58.95 | 55.16 |
| Myrobalans, pulp, another sample | 9.59 | 57.20 | 53.43 |
| Myrobalan extract made at Dehra Dun | 11.19 | 52.16 | 51.56 |
| Gambier (3.56 per cent. ash) | 9.83 | 60.40 | 56.00 |
| Commercial Katha from Daltra Bazar* | 5.02 | 17.63 | 21.95 |
| *Terminalia tomentosa* bark | 7.81 | 10.41 | 10.96 |
| Babul pods with seeds | 10.64 | 10.70 | 8.02 |
| Babul (*Acacia arabica*) bark | 9.41 | 13.31 | 11.66 |
| Pulp of fruits of *Zizyphus xylopyra* | 10.50 | 31.31 | 30.00 |
| *Cassia fistula* bark | 7.91 | 14.09 | 12.45 |
| *Rhus cotinus* leaves | — | 13.57 | 10.57 |
| *Rhus cotinus* leaves, a poorer sample | 10.73 | 5.49 | 6.33 |
| *Rhus cotinus* leaves, another sample | 11.26 | 5.27 | 6.29 |
| *Rhus cotinus* leaves, another autumn sample from young tree | 9.76 | 16.54 | 13.32 |
| *Rhus cotinus* leaves, from old tree | 10.30 | 25.28 | 21.48 |

From these results we conclude that instead of nickel hydroxide paste, as originally proposed, the nickel hydroxide should be used in the form of powder. All other precautions as to extraction and the concentration of tan liquor remain the same; instead of hide powder 20 grams of nickel hydroxide free from water

*A sample heavily adulterated with clay (65.65% ash).

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should be added for detannization. Only in the case of Babul pods it was seen that the nickel tannate formed was in such a minute state of division that it would not settle, and the filtrates obtained were somewhat turbid. This was overcome by mixing the filtrates with well dried kaolin and passing once more through fresh filters.

We are using this method of tannin estimation in this laboratory, and we consider that it is as reliable as the hide powder method, perhaps preferable to it, considering that nickel hydroxide is unlike hide powder a standard substance, and that this method can be used in all cases where organic and mineral acids likely to dissolve nickel hydroxide are not present.

## Discussion.

Mr. J. T. Wood asked Professor Procter what advantage, if any, nickel hydroxide had over sprouted alumina; the latter was a definite compound, and seemed to absorb tannin and reject gallic acid; that was what was wanted.

Professor Procter said that however excellent nickel hydroxide might be as an absorbent material, it was hardly worth discussing, at least for commercial purposes, as the method could only be empirical and the hide powder method under present conditions had firmly established itself as an empirical commercial method, and also had the advantage, perhaps not very real but appealing to the tanner, that it attempted to be an actual tanning process on a small scale. Nickel hydroxide was not by any means the only material which could be used successfully in a similar way. In 1904 Professor H. Wislicenus (see *J. S. C. I.*, 1904, 765), prepared aluminium hydroxide by treating the metal with a trace of mercuric chloride, with which he obtained results probably as satisfactory as those with nickel hydroxide, but which for the reasons cited above never came into use. Probably also other hydroxides might be substituted in the same way. Nickel hydroxide seemed to be inferior to hide powder as regards distinguishing gallic acid from tannin, though neither was particularly satisfactory in that respect. Some of the results with particular tannins and with mixtures of tannin and gallic acid also appeared to be anomalous. But if nickel hydroxide were more easily obtained in remote districts than hide powder, there seemed to be

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no reason why the method should not be used as a preliminary one in forming a judgment for forestry purposes. A method was quoted, but without reference, for the determination of tannins with copper which also appeared, at least in the cases noted, to give satisfactory results. It had long been known that copper methods with certain tannins were capable of considerable concordance and accuracy, but a large class of tannins gave precipitates which were soluble in ammoniacal copper solutions, and for which therefore these could not be used. It was possible, however, that some copper salt of a suitably weak acid, or copper sulphate mixed with a neutral salt of such an acid, might be used direct to precipitate tannins, and if a method of that sort could be found which would give rapid, if even only approximate results, it would be of great value in the practical control of the tanning process, for which a rapid method was much wanted, even if it were quite unsuitable for the commercial analysis of extracts. On theoretical grounds he was extremely doubtful whether most of the tannins were capable really of forming definite salts at all; certainly most of the compounds should rather be regarded as colloidal precipitates than as true salts in the ionic sense.

Mr. Wilkie referred to the paper by D. B. Dott (this JOUR., 1916, 26), in which the use of copper salts was advocated.

Mr. Wood said that the only criticism Mr. Dott had made was that two chemists did not get identical results. The results appeared to show satisfactory concordance in the case of sumac, although the extraction appeared to have been at fault. In a paper which he (Mr. Wood) had read at Brussels some years ago, he showed that it was impossible to obtain identical results because the colloidal precipitate varied.

Professor Procter said that an ingenious method had been suggested at one of the meetings of the Leather Chemists' Association, in which the tannin solution was put in an aluminium basin and an alternating electric current passed through the basin, producing alumina; it appeared to give very satisfactory results as compared with other methods, including the hide powder method. Sumac was an extremely difficult material to extract satisfactorily.

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## EXPERIMENTS IN VACCINATION AGAINST ANTHRAX.*

*By Adolph Eichhorn,*

*Chief of the Pathological Division, Bureau of Animal Industry.*

Anthrax is a disease that is widely spread throughout the world, and in the United States it is being recognized as one of the most destructive scourges of live stock. In certain sections it is more prevalent than in others, particularly in the Southern States, and since no determined effort has been made toward its suppression it appears to be on the increase, its presence now being recorded in localities where it has never before been recognized.

As the spores of the causative agent of anthrax retain their virulence and remain lodged in the soil in an active state for many years in the infected localities, it is very difficult to prevent the spread of the infection, and the eradication of the disease is thereby rendered a most serious problem.

Various factors have to be considered in the prophylactic control of anthrax, such as the prevention of the continued impregnation of the soil with the virus by the proper disposition of the carcasses of animals that have died of the disease, the destruction of the virus contained in the soil by its proper drainage and cultivation, and the prevention of outbreaks through the immunization of the susceptible animals.

In order to attain the greatest success in the control and eradication of the disease, it would appear that the best results can be accomplished only through proper attention to all of the above factors. The execution of these measures would require the earnest co-operation of the stock owners, but even then, on account of the peculiar geographical conditions of certain parts of the country, the drainage and cultivation of the land would not always be feasible, and our efforts must therefore be directed principally toward the sanitary measures and protective vaccination. The enforcement of proper sanitary police regulations in connection with the control of anthrax would no doubt effect a material reduction of the disease, but unfortunately it is rather a difficult task to obtain the co-operation of the interested parties.

* U. S. Dept. of Agriculture, Bulletin No. 340, Dec. 27, 1915.

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The proper disposition of the infective material, particularly the carcasses, should be considered of the utmost importance, since such material constitutes the greatest source of danger toward the spreading of the disease. Drainage from the soil polluted by infected carcasses may carry the infection to distant points and deposit the spores over large areas hitherto uninfected. Buzzards and other birds (Dalrymple), dogs, and even flies may also carry the infection from such sources into uninfected localities. Therefore, in an effort to control the disease, an educational propaganda must be carried out and stringent compulsory measures adopted for the proper disposition of the infective material from premises where the disease appears among the stock.

### Protective Vaccination.

A material reduction and a checking of the disease may be successfully accomplished by periodical vaccination of all stock in infected localities. This method, even if practiced alone, would have splendid results in minimizing the losses from the disease in anthrax localities. However, such vaccination must be carried out regularly and irrespective of whether the disease has already appeared on the premises.

Fortunately we have at our command various methods of vaccination which have proved highly efficient in the production of immunity from anthrax. As a matter of fact, this was one of the first infectious diseases in which protective vaccination was successfully demonstrated, and we are indebted to Pasteur for devising the procedure of the vaccination for this purpose. Pasteur proved that anthrax bacilli when cultivated at a temperature of from 42° to 43° C. will gradually lose their virulence, and also that when removed from such an attenuating temperature and cultivated under normal incubation temperature they will not change their pathogenicity. Thus cultures attenuated for 24 days will be pathogenic for mice but not for guinea pigs and rabbits, whereas if attenuated for only 12 days at the higher temperature they will be virulent for mice and guinea pigs but not for large rabbits. The attenuated cultures will retain their reduced virulence under ordinary conditions, and only in very exceptional instances has any increase of virulence been observed. This

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characteristic of the anthrax bacillus led Pasteur to employ the attenuated forms of the anthrax cultures for vaccination purposes. Accordingly he prepared a weakened vaccine from cultures which had been attenuated for 24 days (*premier vaccin*), and for a second injection cultures which had been attenuated for 12 days (*deuxième vaccin*). In the epoch-making demonstration at Pouilly le Fort, before a commission appointed by the French government, he successfully demonstrated its effectiveness on sheep and cattle. In this instance the vaccinated animals withstood the injection of virulent anthrax bacilli, whereas the controls died. Since that time vaccination against anthrax by the Pasteur method has been very extensively employed throughout the world. Many millions of animals have been vaccinated by this method, and the results in general must be considered very favorable.

At the same time it must be acknowledged that in vaccination by the Pasteur method it is essential to have a potent vaccine and one which is properly tested for its pathogenicity. There are disadvantages in this method of vaccination and these must be given due consideration. The unstable keeping quality of the Pasteur vaccine is a very important factor to be considered. Experience in this line has proved that Pasteur vaccine may deteriorate within a very short time after its preparation, and this has also been demonstrated during the work of the Bureau of Animal Industry in the control of the manufacture of biological products, when periodical tests were undertaken with those of various manufacturers. In repeated instances a vaccine proved inert within three months of its preparation. At other times it remained potent for a period of a year. This no doubt is due to the method of preserving and handling the product. When exposed to light and warm temperature it deteriorates very rapidly, and when it is considered that the products of manufacturers may be stored under unfavorable conditions in branch houses and on the shelves in rural drug stores the loss of potency can be readily explained. For this reason it seems wise to reduce the time limit for the use of Pasteur anthrax vaccine to three months from the date of its preparation.

The injection of an inert product into animals would impart to

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the stock owners and veterinarians who employ it a false sense of security and would bring this method of vaccination into disrepute. At times no doubt great losses have resulted from the application of inert vaccines.

Other disadvantages of the Pasteur method which must be considered are, first, that it requires two handlings of the animals before immunity is established; second, that the losses from vaccinations are not insignificant; third, that its standardization is not carried out very accurately; and, fourth, that its administration in herds where the disease has already made its appearance is liable to induce the disease, through the reduction of the resistance of the animal during the process of vaccination, and for this last reason it is best adapted for use only with herds in which the disease has not yet appeared.

These deficiencies of the method have been recognized by many investigators, who have endeavored to devise other methods of vaccination, and particular attention has been directed toward the preparation of a spore vaccine, because of its superior keeping qualities. In Russia at the present time the method of Zenkowsky, and in Hungary a spore vaccine prepared by Detre, are being successfully employed; although, aside from their keeping qualities, these products have all the other disadvantages of the Pasteur method. Successful vaccination by spore vaccines was also demonstrated by Nitta, in Japan, and by others. Other means of vaccination with attenuated living cultures, aggressions, dead bacteria, etc., were tried, but proved of no advantage.

Sclavo, Sobernheim, and others have established that injections of increasing amounts of virulent cultures into immune animals produced a serum which has great protective value against anthrax. Such protective serum may be produced in the various susceptible animals.

### Production of Serum.

The animals which are selected for the preparation of serum are subjected to a preliminary treatment either by sero-vaccination or by Pasteur's method, then at certain regular intervals they are infected with increasing doses of virulent anthrax cultures. For this purpose they receive in about 10 to 14 days following

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the preliminary treatment an injection of from 0.005 to 0.001 of a loopful of virulent culture. In sheep it is advisable to exercise greater care, especially at the first injection of virulent material, when a very small quantity of culture should be employed, whereas in cattle and horses it is not necessary to employ less than 0.005 of a loopful. The first injection of virulent culture is usually followed by a considerable reaction, inasmuch as the animals usually develop a febrile condition which persists for several days. The subsequent inoculations are then carried out at intervals of from 2 to 3 weeks in such a way that the dose is soon increased to a loopful, then to several loopfuls, and gradually to several agar cultures, and, finally, to an injection consisting of several large mass cultures. This is quite easily accomplished in cattle and horses, and in 3 to 4 months the animals may become so tolerant to this injection that they will withstand the subcutaneous inoculations of two to three mass cultures without noteworthy reaction. At times considerable extensive local infiltration may follow the injection, which, however, retrogresses within a short time and the general condition of the animals is only slightly influenced. In sheep the immunization causes greater difficulties on account of a greater susceptibility of these animals, and it is difficult to prevent a very small percentage of the animals which are being used for serum production from dying in the course of the hyperimmunization. Nevertheless it is possible, even in sheep, to produce such an immunity that they will withstand the injection of several mass cultures without reacting.[1]

The more virulent the strain of the anthrax culture which has been used for the treatment of the animals the more care must be exercised in the course of the hyperimmunization, but in that case the anthrax serum would also be more potent. Therefore, it is advisable to use anthrax strains which have been recently obtained from fatal infections. It is also advisable to use strains of different origin for the immunization. It is immaterial whether bouillon cultures are used or suspensions from agar cultures, but it is more practical to use the latter method for the in-

[1] Bureau of Animal Industry Bulletin 137, "Anthrax, with special reference to the production of immunity," by Charles F. Dawson. 1911, See p. 43.

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oculating material, since in this instance the quantity of fluid to be injected may be limited to a relatively small amount. Quantities of 500 to 1,000 cc. of the bouillon cultures cause, as can be readily seen, considerable technical difficulty for injection, whereas the suspensions from four or five mass cultures may be readily distributed in 50 to 60 cc. of fluid. Fresh cultures which have been cultivated for about 24 hours at 37° C. are as a rule more suitable for inoculation, whereas older cultures with pronounced spore formations possess no advantages over the young cultures.

The inoculations should be made subcutaneously. Intravenous injections as first employed by Sclavo are less effective. The potency of the anthrax serum is in no way increased by this method of immunization. Besides there exists the danger of emboli when in the later stages of the immunization process larger amounts of culture material have to be administered. Animals which have been treated with subcutaneous injections will produce finally an anthrax serum of remarkably high potency.

As a rule the animals which have received one to two agar cultures show a specific protective action of their serum, but for practical purposes it is not advisable to use such a serum. Generally only when the animals stand one-half to one mass culture is the potency of the serum sufficiently strong. A similar condition is manifested in animals used for the production of immune serums for other diseases, the individuals showing a varying response to the injection for the production of immune bodies, *i. e.*, an animal will at times produce a potent serum relatively early, whereas another with the same method of treatment will develop a serum of the same potency only after a considerably longer preparatory treatment. Accordingly, from observation it has been noted that sheep produce the most potent serum, and in this species of animals the individual differences are of almost no consequence, so that almost every animal produces a good anthrax serum. Horses also produce a potent serum, although single individuals may show great variations. The anthrax serum from cattle is quite potent, but in its protective value it does not equal horse and sheep serum.

It is best to draw the blood 14 to 16 days after the last in-

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jection; an earlier bleeding should be avoided. Not infrequently it occurs that animals after an apparent recovery following the inoculation reaction and after a period in which they are free of fever on the eighth or ninth day suddenly develop a rise in temperature. This has been established by Sclavo and Burow. Then, again, repeated regular blood examinations showed that at this time and even later, up to the tenth and eleventh days following inoculation, occasional anthrax bacilli may appear in the blood of the animals in greater numbers.

The bleeding is carried out in the ordinary way, and the blood is collected in large sterilized glass cylinders or similar receptacles of about 2 or 3 liters capacity. Seven or eight liters of blood may be drawn from cattle, about the same quantity from horses, and about 1 to 1½ liters from sheep. After 2 or 3 days another bleeding is made. In this instance, however, only a small quantity of blood should be drawn. The animals resist these operations very readily, and after a lapse of 14 days they are ready for another injection, which is then followed in from 14 to 16 days by repeated bleedings. Thus, in the period of a year, the same animals may be bled 10 to 11 times, and such animals can be used in this way for several years, alternating the injections with the bleedings, provided they are kept in a well-nourished and healthy condition.

In order to obtain the largest possible yield of serum from the blood drawn into the glass cylinders a weight is attached to the same and released onto the clotted blood in about 12 hours after being drawn. The diameter of the weight is about half an inch less than the cylinder and its weight is about 2 pounds. In about 24 hours the clear serum is then siphoned into sterile bottles and preserved with 0.5 per cent. of carbolic acid. If proper precautions have been practiced, it is not necessary to pass the serum through Berkefeld filters; however, if there is the slightest doubt as to its sterility, it is desirable to filter the serum before bottling. It is advisable to distribute the serum in various-sized brown bottles, which should be securely corked and paraffined.

### Standardization of the Serum.

The testing of the serum must be carried out primarily to

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determine its potency. It is to be regretted that for this purpose there are no accurate or definite methods known, and it is almost impossible to establish the absolute protective value of the serum, because the animals on which it is being tested are so very highly susceptible to the disease. Nevertheless, it is possible to establish a relative value for all practical purposes through laboratory experiments, and some investigators believe that rabbits are best adapted for the purpose. The standardization test as recommended by Sobernheim is still employed by various investigators. This test is carried out as follows:

*Potency test for anthrax serum* (*Sobernheim*).

| Rabbit | First injection | Second injection |
|---|---|---|
| A | 2 cc. of immune serum (intravenous) | Follow immediately by a subcutaneous injection of 0.001 loopful of a suspension of virulent anthrax bacilli in 1 cc. of 0.7 per cent. sodium-chloride solution. |
| B | 3 cc. of immune serum (intravenous) | |
| C | 4 cc. of immune serum (intravenous) | |
| D | 5 cc. of immune serum (intravenous) | |
| E | 6 cc. of immune serum (intravenous) | |
| F (control) | 0.001 loopful of a suspension of virulent anthrax bacilli in 1 cc. of 0.7 per cent. sodium-chloride solution. | |
| G (control) | do. | |

According to extensive experience, a serum is considered potent and satisfactory for immunization purposes when at least two of the five rabbits given the serum remain alive and the others die later than the control animals. Should more than the two animals remain alive, while the control animals die in about 48 hours, the serum has an extraordinary potency. It should be noted that it does not follow that those rabbits which receive the smallest serum doses should die, since not infrequently they may remain alive when the rabbits receiving larger doses succumb.

This method of standardization has not been proved as accurate and reliable as the test recommended by Ascoli, and which has been employed in the experimental work with serum prepared in connection with our experiments. In this test a 24-hour-old attenuated bouillon culture is used, which is of such virulence that when introduced subcutaneously in a 0.25 cc. dose into 350-gram guinea pigs it will kill them in from two to three days. These test cultures must be previously standardized in such a way that they will kill guinea pigs which 24 hours pre-

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viously have been injected intraperitoneally with 2 cc. of normal serum. Guinea pigs treated in the same manner and with the same dose of titrated standardized immune blood serum must remain alive.

The testing of the serum is carried out on six guinea pigs, each receiving intraperitoneally 2 cc. of the serum to be tested, and 24 hours later the established dose of the test culture is injected subcutaneously in the axillary region. The serum is considered satisfactory for immunization purposes if at least four of the guinea pigs remain alive over six days while the control animals die within three or four days. For protective and curative purposes in man, only such serum should be selected which, by carrying out the same conditions of the test, protect the guinea pig in 0.5 to 1 cc. doses.

## Experimental Data.

### *Hyperimmunization of Horses.*

On September 8, 1914, two horses, Nos. 48 and 96, were vaccinated against anthrax according to Pasteur's method. On September 29 these two horses were given approximately 0.01 of a loopful of virulent anthrax bacilli subcutaneously. Horse No. 48 showed no apparent reaction following the injection. Horse No. 96, however, developed local anthrax at the point of inoculation. The swelling became enlarged and there was a considerable area of edema below the same. This condition persisted for approximately a week, and finally disappeared. The animal, however, showed no appreciable rise in temperature during this period.

The following table gives in detail the process of hyperimmunization:

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*Hyperimmunization of horses Nos. 48 and 96.*

| Date | Amount of virus given each horse | Result |
|---|---|---|
| 1914 | | |
| Sept. 29 | 0.01 loopful | No apparent reaction in horse 48. Horse 96 developed anthrax at point of inoculation; large swelling; edema of neighboring tissue. Persisted about one week. |
| Oct. 24 | 1 loopful | No noticeable reaction in either animal. |
| Nov. 15 | 10 loopfuls | Do. |
| Dec. 9 | 5 cc. of an emulsion, representing one-half growth of agar culture. | Horse 48 showed a temperature of 102.2° the following day; horse 96 101°. Both animals developed as mall, hard nodule at point of inoculation. |
| Dec. 29 | 20 cc. of emulsion representing washing of growth from 2 agar cultures. | Both animals developed small abscess at point of inoculation. |
| 1915 | | |
| Jan. 19 | 30 cc. of emulsion, growth from 8 agar cultures. | No reaction. |
| Feb. 6 | 40 cc. of emulsion, growth from 2 mass cultures from flasks, surface area 6 by 2½ inches. | Slight reaction in horse 96. Horse 48 showed quite an intensive reaction, developing a large swelling at point of inoculation; persisted several days. |
| Mar. 5 | 50 cc. of emulsion, growth from 4 mass cultures from flasks, surface area 6 by 2½ inches. | No apparent reaction. |
| Mar. 31 | 50 cc. of emulsion growth from 8 mass cultures from flasks, surface area 6 by 2½ inches. | Slight local reaction in each case. |
| Apr. 19 | do | Do. |
| Apr. 28 | do | Slight rise in temperature in both cases. |
| May 11 | do | Slight temperature and local reaction. |
| May 24 | do | Do. |
| June 12 | do | Slight local reaction. |

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In the above work four strains of anthrax bacilli were used, known to us as "Davis," "6071," "Burt," and "Boener"—the first two strains being highly virulent types and the latter two very much weaker. In all cases where the larger amounts of the virus were given the injections were made at 4 to 6 different points in order to minimize abscess formation.

It might be well also to state here that the irregularity in the time between injections was due to the fact that this work was interfered with by the outbreak of foot-and-mouth disease in this country, and for this reason it was also impossible to subject the blood to periodical tests to ascertain its immunizing value at the different intervals between injections. Experience proved that horses may produce highly potent serum following the injection of the first or second mass cultures. It is therefore advisable to subject the blood of the animals to periodical tests for potency throughout the course of immunization.

On June 25, 1915, 6 liters of blood were drawn from each horse into the glass bleeding cylinders previously described. Since this date these animals have been bled regularly, 6 liters being taken from each horse, and an injection of virus made in the intervals between bleedings.

*Serum Tests.*

In standardizing our serum, that taken from each horse was tested separately. The following procedure was carried out: Three series of guinea pigs were inoculated intraperitoneally with varying amounts of serum, and 48 hours later were injected with 0.25 cc. of a 24-hour bouillon subculture of an attenuated strain known as "Davis D." This culture had been attenuated by growing it at a temperature of 42°–43° C. for a period of 20 days. Previous tests of this culture showed that it was uniformly pathogenic for guinea pigs, killing them in two or three days, but it failed to kill rabbits. The results of this test are contained in the following table:

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*Standardization test of anthrax serum (serum injected intraperitoneally; virus 24 hours later subcutaneously).*

SERUM 48.

| Guinea Pig No. | Amount of serum | Amount of virus | Result |
|---|---|---|---|
| 1 | 1.0 cc. | 0.25 cc. | Remained alive. |
| 2 | 1.5 cc. | 0.25 cc. | Died on third day. |
| 3 | 2.0 cc. | 0.25 cc. | Remained alive. |
| 4 | 2.5 cc. | 0.25 cc. | Do. |
| 5 | 3.0 cc. | 0.25 cc. | Do. |
| 6 | 3.5 cc. | 0.25 cc. | Do. |

SERUM 96

| | | | |
|---|---|---|---|
| 1 | 1.0 cc. | 0.25 cc. | Remained alive. |
| 2 | 1.5 cc. | 0.25 cc. | Do. |
| 3 | 2.0 cc. | 0.25 cc. | Died on third day. |
| 4 | 2.5 cc. | 0.25 cc. | Remained alive. |
| 5 | 3.0 cc. | 0.25 cc. | Do. |
| 6 | 3.5 cc. | 0.25 cc. | Do. |

NORMAL HORSE SERUM.

| | | | |
|---|---|---|---|
| 1 | 1.0 cc. | 0.25 cc. | Died on fourth day. |
| 2 | 1.5 cc. | 0.25 cc. | Died on third day. |
| 3 | 2.0 cc. | 0.25 cc. | Died on fourth day. |
| 4 | 2.5 cc. | 0.25 cc. | Remained alive. |
| 5 | 3.0 cc. | 0.25 cc. | Died on fourth day. |
| 6 | 3.5 cc. | 0.25 cc. | Died on third day. |

In view of these results it was decided to use the "Davis D" culture in the preparation of our spore vaccine, to be used simultaneously with the serum.

Extensive tests to determine whether or not the immune serums possessed a bactericidal property proved negative.

## Preparation of Spore Vaccine.

The four cultures used for the hyperimmunization of the horses were attenuated at a temperature of 42.5° C. for varying periods. From time to time they were tested for their pathogenicity by inoculation into mice, guinea pigs, and rabbits. The cultures, which were removed from the incubator after 20 days of attenuation, proved satisfactory for the purpose, inasmuch as the test inoculation demonstrated their virulence for the mice and guinea pigs, but not for rabbits.

For the purpose of producing a spore vaccine it is desirable to use a peptone-free agar medium and after inoculation with the

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attenuated culture to grow the organisms at a temperature of 37.5° C. for 4 to 7 days, by which time an abundance of spores will have formed. The growth is then washed from the slants and collected in a sterile flask and heated at a temperature of 60° C. for one-half hour, to destroy the vegetative forms of the organism. A measured quantity of this suspension can then be plated out in the usual manner and the spore content of 1 cc. of the suspension established. A dilution can then be made to the desired amount for inoculation purposes. Thus, if it is desired to use for vaccination 1,000,000 spores, it is best to dilute the vaccine to a quantity of which 1 cc. would contain this number. Of such vaccine 1 cc. would constitute the dose for cattle and horses, with correspondingly smaller doses for calves and sheep.

In all forms of vaccination against anthrax in sheep the greatest care must be exercised, since these animals are very susceptible to the disease, and at times vaccines which have no ill effects on cattle will prove fatal to sheep; therefore the dose of the spore vaccine for sheep should not be more than one-fourth the amount given cattle.

In the preparation of spore vaccines it is essential to submit every lot to a test for pathogenicity by inoculating approximately 250,000 spores—that is, 0.25 cc. of the standard suspension—into guinea pigs and rabbits before employing the same for vaccination purposes. The guinea pigs should die in from 2 to 5 days, whereas the rabbits should remain alive.

In consideration of the keeping qualities of the spore vaccine, large lots can be prepared without fear of deterioration. In the bottling and storing of the same, however, proper care should be taken to prevent contamination.

### Technic of Administration.

For immunization purposes by the simultaneous method the serum should be injected first. It is desirable to divide the herd into groups of 10 or 12 and inject first each animal of the group with the serum, following this with the injection of the spore vaccine. The serum should be injected on one side, either on the neck or back of the shoulder, and the spore vaccine on the other side, the injections being made subcutaneously.

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In herds where the disease has already made its appearance it is necessary to take the temperatures of all the animals and to subject to the simultaneous vaccination only those that show no rise in temperature. All others should be given the serum-alone treatment in doses varying in accordance with the severity of the symptoms manifested by the individual animals. If the examination reveals a considerable number of infections, it is advisable to use the serum alone for all the animals, and in 3 or 4 weeks to revaccinate by the simultaneous method.

The dosage should depend on the potency of the serum, serum of a high potency naturally being most desirable; thus, in some instances serum in 5 cc. doses for large animals and 3 cc. for smaller ones was found to be effective for immunization purposes. Unfortunately all hyperimmune animals do not yield serum of such high potency, and for this reason it is obvious that accurate potency tests should be carried out by the producer of the serum.

In the treatment of anthrax, serum should be administered in large doses. An animal showing only a high temperature, with no other manifestations of the disease, should be given from 30 to 50 cc., but if the gravity of the disease is pronounced, 100 cc. should be administered. In almost every instance a drop in temperature may be observed and a diminishing of the severity of the symptoms. At times, however, a relapse occurs about the second or third day following the serum injection, when it becomes necessary to administer another dose of serum. It has been proved that animals affected with anthrax, even after the bacilli are found in the blood circulation, may recover after an injection of potent serum.

The simultaneous treatment, as in the Pasteur treatment, may at times result in a temperature and systematic reaction in the animals. These manifestations are indicated by an elevation of temperature and sometimes by a swelling at the point of inoculation of the spore vaccine. These symptoms, however, are usually of short duration, and only in very exceptional cases will they result in the loss of the animal. However, if the reaction following the injection of the spore vaccine threatens the life of the animal, a second injection of serum should be administered.

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The anthrax serum injected simultaneously with the vaccine has a counteracting effect upon the reaction which may follow the injection of the spore vaccine during the process of immunization.

At times anaphylactic reactions are observed as a result of the serum injected, especially in cases where the serum is foreign to the animals treated. These manifestations appear as a rule within one-half hour after injection, in the form of urticarialike eruptions, swelling of the head, slight chills, and rise in temperature. More severe symptoms have also been noted to follow such injections, but they almost invariably subside within a few hours.

### Test of the Simultaneous Method on Cattle and Sheep.

A series of experiments was conducted at the experiment station of the Bureau of Animal Industry at Bethesda, Md., to establish the efficiency of the simultaneous method of anthrax immunization on cattle and sheep.

For this purpose 6 head of cattle and 5 sheep were given the simultaneous injection of anthrax serum and spore vaccine. Three weeks subsequent to immunization they were subjected to infection tests which consisted of a subcutaneous administration of 0.25 cc. for the cattle and 0.125 cc. for the sheep of blood from a guinea pig which had died from an artificial infection with our most virulent strain of anthrax.

The microscopic examination of the blood of the guinea pig showed it to be heavily charged with anthrax bacilli, but in order to make the test as severe as possible it was deemed advisable to use such excessive amounts. Three additional cattle and two sheep were used as checks, receiving only the virulent blood. As a result of this infection all animals manifested an elevation of temperature ranging from 103° to 107° F. The control animals especially were markedly affected with typical manifestations of anthrax and all succumbed within two to eight days following infection. All but one of the vaccinated sheep succumbed to anthrax, but at a later date than the check animals. Of the immunized cattle a marked temperature reaction was noted, but all of these animals recovered with the exception of a small, undersized, weak calf, which died in six days following infection.

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While in the above test the sheep succumbed and one of the small calves died of anthrax, nevertheless the potency of the serum was demonstrated. The excessive virulent blood used for the infection was extraordinary and could not be compared with the amount of virus taken by a susceptible animal in cases of natural infection.

## Field Tests.

On June 21, 1915, Dr. R. R. Ashworth, a dairy inspector for the District of Columbia, notified our office that a number of deaths among hogs were occurring on a farm in Maryland, just outside of the District. The symptoms described by Dr. Ashworth pointed suspiciously to anthrax. A visit was made to the farm the same morning, and after an autopsy on several animals, followed by a bacteriological examination, a definite diagnosis of anthrax was established. This was later conclusively verified by animal inoculation tests.

At that time 7 shoats and 4 sows had died of the disease and 3 shoats, 4 sows, and 1 boar were showing symptoms of anthrax, several of the sick animals manifesting the characteristic edema of the throat region. It is desired to make particular mention of the boar, a fine pure-bred animal, which was in an almost comatose condition, showing a profuse bloody diarrhea, and a temperature of 106° F. One of the sows was also in a very critical condition.

On the afternoon of June 21 the affected animals were given injections of the immune serum, the boar receiving 100 cc., the sows 50 cc., and the shoats 30 cc. On the following day a visit was made to the farm to immunize the remaining hogs, which as yet had shown no symptoms of the disease. A total of 138 were given protective doses of the serum, the larger hogs weighing 75 pounds or over receiving 10 cc. and the smaller animals 5 cc. Marked improvement was noted in the sick animals that had been treated the day before.

On June 23rd another visit was made to the farm. All of the sick animals showed still further improvement. The boar was given 60 cc. more of immune serum and the sow that had been the most sick was given an additional 30 cc.

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The result of this work was that every affected animal recovered, and up to the present time not a single death from anthrax has been reported in those animals that received protective doses of the serum.

In the early part of July an outbreak of anthrax was reported from Queen Anne County, Md. On July 13th two inspectors from the bureau were detailed to make an investigation, with a view to using our immune serum and spore vaccine in an effort to control the outbreak. The disease had made its first appearance about a month previous to this time, when a farmer lost a cow from anthrax. A few days later a neighbor on an adjoining farm lost a hog from the disease. Following this, the disease made its appearance on five other farms in the immediate vicinity, the greater percentage of animals stricken dying of the apoplectic form of the malady. Animals on some of the farms had been treated with single injections of a commercial vaccine before the arrival of our inspectors. Immunization tests were at once started with the bureau serum and spore vaccine, with the following results:

The animals on six farms where losses had occurred from anthrax were vaccinated, the cattle, horses, and mules receiving 10 cc. each of serum and 1 cc. of spore vaccine, except, however, in cases where there was reason to believe an animal might be in the incubative stage of the disease, when the vaccine was omitted and the dose of serum increased. Sheep and hogs on the infected farms were given the serum-alone treatment, receiving from 5 to 10 cc. each.

On the day subsequent to vaccination a mule on one of the farms showed symptoms of anthrax, there being an elevation of temperature and a characteristic swelling on one side of the neck, the side opposite to where the vaccine had been injected. This animal was given an injection of 60 cc. of serum and made a speedy recovery.

In all, 399 animals, including horses, mules, cattle, sheep, and hogs on farms where the disease had broken out, were treated with the bureau serum and vaccine. Previous to this an aggregate of 10 cattle, 3 mules, and 13 hogs had died of anthrax on these farms. On the morning of the day following vaccination

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a cow on one of the farms died of anthrax. Exclusive of the above, no losses from anthrax have occurred on any of these farms.

Approximately 140 animals on several other infected farms were vaccinated with a commercial vaccine by a representative of the State live stock sanitary board. Within a day or two following this vaccination it was reported 3 cows and 1 mule died of anthrax, and since then 2 more cows have died of the disease.

Another opportunity was afforded us to test the serum and vaccine in an outbreak of anthrax in Noxubee County, Miss., where a number of farms were reported to be infected with the disease. A quantity of serum and spore vaccine was furnished, and an inspector detailed from the bureau station at Birmingham, Ala., to conduct the work. On various farms where the disease had made its appearance a total of 125 cattle were given the simultaneous treatment. In addition 3 animals which showed symptoms of the disease were given 30 cc. of serum alone. No deaths from anthrax occurred immediately following or since the vaccination, the affected animals having all recovered from the disease.

### Use of Serum in Treatment of Anthrax in Man.

Extensive data are available on the effectiveness of anthrax serum for the treatment of the disease in man. It is recommended that from 30 to 40 cc. of serum be injected in three or four different places. Should no improvement follow in 24 hours an additional injection of 20 to 30 cc. of serum should be administered.

In most instances the results are very favorable, and this treatment is acknowledged to be superior to any other mode of treatment known for this disease.

### Concentration of Serum.

Experiments are now being conducted in drying immune serum with a view to preparing the same in pellet form. For this purpose the serum has been dried in shallow pans in a serum-drying apparatus. After thorough drying it is scraped from the pans, milled into a fine powder, and prepared in a pellet machine into

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proper-sized pellets. The spore vaccine is also being prepared in a similar manner. This procedure would greatly simplify the administration of the serum and vaccine and, besides, the products would be in a form least likely to deteriorate or become contaminated.

The proteids containing the protective bodies of the serum have also been successfully precipitated through fractional saturation of the serum with ammonium sulphate, and further work along this line is now being conducted. However, this work and the work on the drying and concentration of the products are still in the experimental stage, and it is our aim to properly work out a method most suitable for immunization of animals in the field.

## Conclusion.

1. Horses are suitable for the production of highly potent anthrax serum. Serum of such horses should protect large animals in 10 cc. doses.

2. The use of the serum-alone treatment is indicated in cases where the infection has already occurred in a herd. Since the serum confers only a passive immunity, it is advisable to revaccinate the herd in from three to five weeks by the simultaneous method.

3. The serum possesses great curative value. Depending on the severity of the infection, the curative dose is from 30 to 100 cc.; the injection to be repeated if necessary.

4. For the simultaneous treatment a spore vaccine, carefully standardized, is preferable to the ordinary Pasteur vaccine.

5. Spore vaccine should be employed also in preference to the Pasteur vaccines for immunization with vaccine alone. This vaccine has a decided advantage over the Pasteur, because of the possibility of more accurate dosing and because of its better keeping qualities.

6. Experiments with concentrated serum and dry spore vaccine are very promising. This method would greatly simplify the vaccination process and also insure the product against subsequent contamination and deterioration.

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## ABSTRACTS.

**Anthrax With Special Reference to Its Suppression.** HENRY J. WASHBURN. U. S. Department of Agriculture, *Farmers' Bulletin* 439. Three forms of the disease are recognized: apoplectic, acute and subacute. The first is generally met with at the beginning of an outbreak, before animals in the vicinity have developed any degree of natural immunity from the disease. The symptoms are those of apoplexy. The animals reel and fall, bloody liquid flows from the body openings and death soon follows. Examination of the body may fail to show any definite lesions or change in the tissues. In the acute form, the disease develops more slowly, but is well established in from 12 to 24 hours after the first symptoms are noticed. Intense fever (104°-107° F.) and great prostration follow with drowsiness and staggering, bloody urine and convulsions. In this type also postmortem examination may fail to reveal any lesions. The third form of anthrax, the subacute, is the most common. The symptoms are like those of the acute form, but develop more slowly, taking from one to seven days. High fever and acute colic are observed. Tumors appear at points where the skin is bruised or abraded, especially on the head, neck or shoulders. Examination of the carcass shows many changes, including hemorrhage in many parts of the body, swollen spleen, liver and kidneys, and serous infiltrations may be present beneath the skin and mucous membranes. The blood is muddy and not coagulable, and the serum reddened, the red corpuscles being in large part broken down. The subacute form is the only one which can be treated successfully, as the others are so quickly fatal as to afford no opportunity for treatment. Of this form are most isolated or sporadic cases, which are often limited to the tumor at the point where the germs found entrance. The organism which causes the disease (*bacillus anthracis*) is a straight rod, which under favorable conditions develops spores. The rods are easily destroyed by heat or antiseptics, but the spores are very resistant and long-lived. The organism does not develop spores in the absence of air. Pasteur developed a method of immunization from anthrax by means of vaccine treatment as long ago as 1881, and this treatment has been extensively used ever since in regions infected with the disease. The vaccines used for this purpose contain "attenuated" anthrax organisms and are only suitable for use by experienced veterinarians, since mistakes may result in spreading the disease instead of curbing it.

**South American Mangrove.** CONSUL L. B. MODICA, *Commerce Reports*. No bark is being shipped from the Cartagena region, but two factories are making extract, one at Cartagena and one at Cispata Bay. The output of both is now all going to the United States. The price realized has more than doubled since the beginning of the war. The capacity of each factory is about 220 tons a month. The Cartagena factory is equipped with English and French machinery; that on Cispata Bay with American. The extract is shipped in paper-lined nankeen bags, holding about 100

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pounds each. There is said to be an abundance of mangrove in the Bahia district, Brazil, but no bark is being shipped.

**Embargo on Hides in South Africa.** *Commerce Reports.* A telegram from the U. S. Consul General at Capetown, March 4th, states that shipment of wet or dry salted hides has been prohibited, except to Great Britain. Under certain conditions light weight sun-dried hides may be exported.

**Brazil Likely to Consider Mangrove Bark Trade.** Consul General ALFRED L. M. GOTTSCHALK, Rio de Janeiro, Feb. 4, in *Commerce Reports.* The percentage of tanniferous extract usually obtainable from the Brazilian mangrove seems to be about 36 per cent. from the bark and 24 per cent. or less from the leaves. No apparent use seems to be made of this important natural resource here. The chief difficulty appears to be a legal one. Many of the municipalities of Brazil have the fear that if promiscuous cutting of mangrove swamps were permitted the sea would make inroads upon the denuded coastal regions and, besides, that dangers of fever would be present after the deforestation. Another very great, but perhaps not insuperable, difficulty lies in the fact that by law a broad strip of the Brazilian shore, throughout the coast, is reserved to the Government, as a "maritime zone" for purposes of national defense, and that this would include practically the entire habitat of the Brazilian mangrove. It would probably be possible, however, to obtain concession from the Brazilian Government to work certain defined coastal sections. Several persons who have called at the American consulate general have stated that they would be willing to furnish mangrove bark, leaf and wood. The latter is valuable for use as construction material, especially piles and railroad ties, and has, as such, already attracted attention in France. Mangrove bark is not exported from the Sao Paulo district, although the mangrove tree is found in various sections. The bark consumed in the local tanneries is secured in the market of Buenos Aires.

**Cutch for Tanning and Dyeing.** Consul GEORGE M. HANSON, Sandakan, British North Borneo, Jan. 5, in *Commerce Reports.* The manufacture of cutch in Borneo has progressed in a few months from an industry that barely paid expenses to one of considerable importance. The operating company is a Scotch firm with headquarters at Glasgow. It now possesses a factory at Sandakan and another at Kudat. The sudden demand for cutch arises chiefly from the current shortage in coal-tar dyes, due to the cessation of supplies from Germany. While cutch is largely employed for tanning, it has an equally extended use as a dyeing material. It is frequently employed in combination with other natural dyes and also with coal-tar colors. Large amounts are required in the dyeing of cotton and silk fabrics; thus far the application to woolens is very limited.

The varieties of cutch found in commerce are gambier cutch (terra

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japonica) obtained from the leaves and twigs of the *Unicaria gambier,* Bombay cutch from the fruit of the *Areca catechu,* Bengal cutch from the heartwood of the *Acacia catechu,* and mangrove cutch from the bark of *Ceriops candolleana,* as well as from varieties of *Rhizophora.* The three forms first mentioned above are those which hitherto have found an extensive application in the dyeing of cottons, either to produce directly the very fast color known as "catechu brown," or to bring out compound shades with fustic, logwood, alizarin, etc., in combination with such an oxidizer as potassium bichromate, or directly, with bismarck brown, magenta, and allied artificial colors. In silk dyeing cutch has served chiefly as a "weighting" material.

Mangrove cutch has been employed hitherto almost exclusively for tanning purposes. Its availability for use in dyeing, in much the same way as gambier, etc., has recently attracted attention, as the demand for cutch in other forms has materially increased.

The mangrove is usually found in immense jungles on swampy ground along the seashore and about the mouths of rivers in all tropical countries. There are two distinct kinds of mangrove here. The ordinary kind is known by the native Malay name Bakau, and that name is also applied to the extract of the bark. The other kind is called Tungah, also a native name. Tungah is decidedly superior to Bakau, as the bark produces a superior quality and a greater amount of extract. Cutch made from Tungah is more valuable for dyeing purposes. It sells for a much higher price than that made from Bakau mangrove.

The factory at Sandakan at present produces about 160 tons monthly. The plant is being increased to a productive capacity of 250 tons or over per month. The supply of mangrove trees in Borneo, as well as in the Philippines and other tropical countries, is practically inexhaustible. The Sandakan factory has secured its supply of bark for 20 years from the immediate vicinity, and the groves are still far from being exhausted. Mangrove jungles renew themselves in 15 to 20 years.

The manufacturing process is exceedingly simple, although some features are kept secret. The freshly gathered bark is tied with rattan in small bundles, weighing 10 or 15 pounds, and boiled in vats until most of the soluble matter has been extracted, evidenced by the density of the resultant decoction. Concentration by evaporation is effected in the same vacuum apparatus as is used ordinarily for refining sugar. When the desired consistency is obtained and the water present does not exceed 25 per cent., the thick residue is drawn off in a plastic state. It is packed in strong bags for short distance shipments and in boxes for transportation to America or Europe. During the cooling process it hardens until it resembles resin. Formerly the bark was broken into small pieces, and even ground, before boiling, but this treatment has been abandoned. The additional extract secured does not cover the trouble and expense of crushing or grinding. The bark, when tied in bundles, can be more easily handled. After boiling, it is also in a convenient shape to be fed into

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furnaces as fuel, after being thoroughly dried. The price of Bakau or ordinary cutch has advanced from £13 to £35 per ton. The price of Tungah has reached £42 per ton. There is at present an embargo on the shipment of cutch except to English possessions, the countries of the allies, America, and Japan. The latter country is buying it in large quantities. The cost per pound for East Indian cutch in New York was 4⅞ cents in February, 1913 and 1914, 5½ cents in 1915, and 14 to 30 cents in 1916. The price for gambier has risen from 4½ cents per pound in 1914 to 17 and 18 cents in 1916. Imports of mangrove bark into the United States during the last four fiscal years were 21,800 long tons in 1912, 15,200 in 1913, 7,700 in 1914, and 8,100 in 1915. The average price per ton in 1914 was $25.60; in 1915, $27. The chief source is Portuguese East Africa. Prior to the war most of the import came *via* Germany. The import from Venezuela and Colombia is about 600 tons annually. The importation to the United States from Colombia of mangrove extract has begun to assume some importance.

**Solution of Russian Tanning Problem.** ANON. in *Shoe and Leather Reporter,* Mar. 11. A special commission on the development of the methods for tanning leather, organized by the Russian Department of Agriculture, in co-operation with the Zemstvos (County Councils) of the Caucasus and Transcaucasia, has just rendered its report. By this report the problem of procuring such supplies during the war has been solved, and moreover, so fruitful has been the investigation that the tanning industry in Russia is placed upon a new basis. Since the beginning of the war and the consequent cessation of tanning supplies, the problem of developing methods for procuring tannin in the country has occupied the attention of all the Russian agencies interested in the question of encouraging the thriving leather industry of Russia. There have always been primitive methods for the tanning of skins used by the peasant artisans, or Koustari, but the methods were of irregular value and the results not always satisfactory. As the government is using every force in its power to build up the Koustar work, these developments in tanning are far-reaching, for experts will be sent into all the villages to train the peasants. The problem of solving the tanning situation on a larger scale was undertaken by botanists attached to the Tiflis Botanical Gardens and to the Caucasian Museum. Several expeditions were undertaken into the region lying east of the Black Sea for the purpose of studying the vegetation of this rugged country, with the view of utilizing it in the making of tanning material. At Tiflis, a chemicobacteriological laboratory was established in the Department of Agriculture. At this laboratory and at one of the private leather tanning factories, numerous experiments were carried on to determine the value of the different methods. The results of the investigations show that the Caucasus is rich in tanning materials. The most valuable regions are in Western Transcaucasia, where sumac, oak and chestnut grow in profusion. Hazel and gatten tree are found throughout, all valuable for tanning. The presence of tannin in such a well-known plant

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as sumac has been definitely established, and 15 to 20 per cent. of tanning material has been found in such plants, which can be prepared in quantities which reach thousands of pounds. The chestnut wood found in Kakhet not only contain as much tannin as in the other parts of Europe, but 2 per cent. more or even a larger proportion. A high content of tannin was discovered for the first time in the leaves of the gatten tree containing sometimes as much as 18 per cent., yet this plant was never before employed in the process of tanning. The laboratory tests of its tanning value were highly successful. The problem of raw material has thus been solved, and now the commission is beginning to superintend the manufacture on a large scale. Already the supplying of sufficient tanning material for leather needed by the army is well in hand, and the question of establishing the industry on a permanent commercial basis is now being studied.

**China Offers Market for American Leather.** Consul G. E. ANDERSON, Hong Kong, in *Commerce Reports.* Imports of leather into Hong Kong average about $2,500,000 yearly. Of this about $1,000,000 represents high grade leathers from Australia, Europe and America. The cheaper leathers have come from Singapore and the East Indies. The rise in price of Australian leathers, due to war conditions, gives American leathers a good chance to compete. Cheap Japanese leathers are being sold more and more extensively. Colors are an important feature in calf leathers, certain tan shades being most in demand.

**Chinese Hides and Skins.** JAMES S. DOLAN, now located in Delhi, India, contributes to *Hide and Leather* under the above title an interesting series of articles illustrated with excellent photographs. Installments appeared in the issues for Sept. 25, Nov. 27, Dec. 11 and 25 and Feb. 19. Travel up the Yangtse Kiang by steamer to Ichang and then by house-boat pulled through the gorges by "trackers" to Chungking, is described most interestingly. There are two firms in Chungking who deal in goat-skins, sending them by boat to Shanghai. The skins are well taken off, and are packed in bales of 300 each for shipment. The dampening of skins to add weight results in some heating on the trip. The writer went from Chungking to Chengtu by chair, over the rough and crooked "roads" which can be traveled by men and pack animals only, being too narrow, rough and crooked for any vehicle on wheels. The goatskins of the Chengtu plain are the best Mr. Dolan saw.

**Wattle Extract Factory in East Africa.** *Commerce Reports.* Owing to the outbreak of war, plans for the erection of a factory for the production of wattle extract at Naivasha, East Africa Protectorate, have fallen through, though planters in that region have not lost interest in the scheme. There are some 7,500 acres under wattle in the Protectorate, states the *Board of Trade Journal,* but high ocean freights render unprofitable the exportation of the bark. Accordingly the planters are awaiting with much interest the results of experiments now being conducted in Natal in connection with the extraction of tannin from the bark.

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**Brazil's Tanning Materials.** The following information as to the vegetable tanning materials available in Brazil is taken from the *Bulletin official du Bureau de Renseignments du Brésil a Paris* (through *Hide and Leather*):

Barbatimao (Stryphnodendron barbatimao, Mart.) is a forest tree belonging to the Leguminosœ, occurring in Brazil from the State of Ceara to Rio Grande do Sul. The bark contains from 25 to 48 per cent. of tannin and has long been used for tanning hides, especially in the States of Sao Paulo and Minas Geraes. Angico vermelho (Piptadenia rigida, Benth.) is a tree also belonging to the Leguminosœ, the bark of which is an excellent tanning material and is used as such principally in the States of Pernambuco, Parahyba and Parana. The tree is abundant in Brazil from the Maranhao to Rio Grande do Sul. Caparrosa (Ludwigia caparrosa, Baill); the bark of this tree, which is abundant in the States of Minas Geraes and Goyaz, contains from 20 to 25 per cent. of tannin. The mangroves, known commonly in Brazil under the name of mangues, belong to various botanical genera and occur on the banks and at the mouths of waterways which are subject to periodical inundations as well as on low-lying sea coasts in swamps of brackish water. Decaying vegetation produces deep slime, which renders access to the manguesaes, as the mangrove forests are called, very difficult. The mangrove forests are prolonged into the interior of the country along the low and flooded banks of the rivers. They are also found on the edge of lakes and lagoons, and generally where there are permanent waters more or less brackish. Mangroves are not uncommon in the valley of the Amazon, but they are particularly abundant on the sea coasts from the State of Para to Rio Grande do Sul, where they frequently occupy continuous areas of several square kilometers. Not only the bark of the various mangroves is used for tanning but also the leaves. The two tanneries in the town of Santos, in the neighborhood of which mangrove forests abound, consume about 1,800 cubic meters of mangrove bark a year. Santos uses also mangrove leaves to the extent of 1,350,000 kilos a year. In the State of Santa Catharina only the leaves of the mangroves are used for tanning. Their consumption amounts to over 400,000 kilos a year. Caporoca (Myrsine gardneriana, D. C.) and the Arveiras (Astronium and Schinus) are very abundant in the State of Rio Grande do Sul and are largely utilized there for tanning ordinary and sole leathers. There are many other plants in Brazil which are more or less rich in tannin, but the superiority in this respect belongs incontestably to Barbatimao on account of its high percentage of tannin and to the mangrove, Rhizophora mangle, L., known as mangue vermelho, which, though it contains no more than 30 per cent. of tannin, is extremely abundant and very easy to exploit.

**Mangrove Cutch in the Federated Malay States.** B. H. F. BARNARD. *Agricultural Bulletin of the Federated Malay States,* Vol. 3, pp. 241-5. The mangrove forests of these states embrace 250 square miles. The kinds of trees found in a given area depend on the soil and on the liability

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to inundation by the tides. Nine species of mangrove, representing six genera, are mentioned. The most abundant are *Rhizophora mucronata* and *R. conjugata.* The former has from 30 to 40 per cent. tannin in its bark, and the latter hardly more than one-fourth as much. The most prized species is *Ceriops candolleana,* the bark of which has from 35 to 40 per cent. tannin. This species is much less abundant than the other two mentioned. Tanning extract has thus far been made in these states only in small quantities for local use. Some 7,000 acres of forest are leased to Chinese cutters who take out about 125,000 tons of firewood a year. The ground is cut over systematically, and so it is likely that an abundant supply of bark for the manufacture of extract will continue to be available indefinitely. At present the bark is a waste product. The health conditions in these forests are good. One acre yields from 4 to 8 tons of bark. Transportation by water is easy, and railroad terminals at Port Weld and Port Swettenham are actually in the mangrove area. The forest leased for firewood contains the species most valued for tannin.

**Oxidation of Sewage Without the Aid of Filters.** E. ARDERN and W. T. LOCKETT. *J. S. C. I.,* Feb. 16, 1916. Discussion of the paper by Ardern and Lockett, an abstract of which appeared in the Dec., 1915, number, p. 647. Dr. G. J. Fowler stated that the city of Milwaukee is now experimenting with the continuous process involving activated sludge, on a scale of 20,000 gallons daily, and proposes to construct tanks capable of dealing with 2,000,000 gallons. Experiments on the fertilizer value of the activated sludge show excellent results. The University of California reports that the nitrogen in activated sludge has as high a degree of availability as that of any other kind of organic manure tested there. Mr. Ardern said in reply to questions that the estimates of cost included a duplicate air plant. The increase in the volume of sludge other than that actually contained in the sewage is so great that until further investigations have been made, he was not prepared to discuss this point. It would not be practicable to reduce the water content by a further period of sedimentation. It is important to notice that the sludge is absolutely non-colloidal in character, and after draining on filters makes a spadable product. It is likely that centrifugal separators will afford the best means for freeing the sludge from water. The figures heretofore given for the nitrogen content of activated sludge are rather lower than may be expected. A recent determination on a sample of domestic sewage showed 6.5 per cent. nitrogen on the dry material of the sludge. The best method of distribution of air through the sewage which has yet been tried is by means of porous plates in the bottom of the tanks. A great deal remains to be learned in regard to the complex biochemical reactions involved in the process.

**Purification of Sewage by Aeration in the Presence of Activated Sludge.** EDWARD BARTOW and F. W. MOHLMAN. *J. Ind. and. Eng. Chem.,* Jan., 1916, pp. 15-17. The authors have carried on investigation of this method of

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sewage treatment at the University of Illinois, Urbana, Ill. Four reenforced concrete tanks 3 feet 2 inches square and 8 feet 5 inches deep have been built for the work. Two of these have the entire bottom made of porous plates through which the air is forced. The third has a strip in the middle embracing one-third of the floor so covered, and the rest of the floor slopes toward the porous part from both sides at an angle of 45°. The fourth has a single plate in the middle, covering one-ninth of the area, and the rest of the floor slopes toward this from all sides at an angle of 45°. The air enters at a pressure just sufficient to overcome the pressure of the sewage in the tanks. If activated sludge is built up by complete nitrification of each portion of sewage added, several weeks would be required to put a plant into operation. The English investigators have used sludge from sprinkling filters in order to obtain an active sludge more quickly. At Milwaukee, sludge from Imhoff tanks has been used. Experiments in regard to the shortening of the process of building up active sludge were tried as follows: The two similar tanks were filled on the same day with the same kind of sewage. That in tank A was aerated continuously, while that in tank B was aerated for 23 hours, allowed to settle, the liquid drawn off and fresh sewage added. This cycle was repeated daily for 10 days. At the end of this time, 1 per cent. of the volume of A consisted of sludge, and 10 per cent. of the volume of B. The effluents were equally stable, but that from B was clearer. Tank B was kept in continuous operation on the 24-hour cycle, and after 15 days, nitrification was complete in the 24 hours. The sewage was then changed every 12 hours, and after 8 more days nitrification was found to be complete in the 12-hour period. The period was then cut to 6 hours, and some of the batches were completely nitrified in this time. Comparison of the three types of tank indicate that the second, having one-third of its floor porous, gives the best results. The quantity of air required after the process is in operation is from 1 to 2 cubic feet of air per gallon of sewage. In order to keep the sludge in its most active condition, either each batch of sewage must be completely nitrified, or the sludge alone must have additional aeration. A completely nitrified effluent is neither necessary nor economical. Effluents are usually stable if 50 per cent. of the free ammonia is removed, and from 2 to 3 parts per 1,000,000 of nitrogen as nitrates are present. Other features which it is proposed to study are the amount of sludge formed, the building up of nitrogen in the sludge and the composition of the effluent gases.

**Fertilizer Value of Activated Sludge.** EDWARD BARTOW and W. D HATFIELD. *J. Ind. and Eng. Chem.*, Jan., 1916, pp. 17-20. Experimental plants using the method of sewage disposal originated by Ardern and Lockett of Manchester, England, and described by them in 1914 are in operation at Baltimore, Chicago, Cleveland, Houston, Milwaukee, New York, Washington, Urbana, Ill., and at Regina, Saskatchewan. At Milwaukee both fill and draw and continuous flow methods are being operated on an experimental scale, and a 2,000,000-gallon plant is being built. At

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Cleveland a 1,000,000-gallon plant is to be built. As in all sewage disposal methods, the disposition of the sludge is of great importance. In the experimental plant at the University of Illinois careful study has been given to the problem of sludge disposal. The amounts formed and their composition vary with the character of the sewage and the temperature conditions. The nitrogen content of the dry sludge varied from 3.5 to 6.4 per cent. The material was subjected to many tests, both by analysis and by growing trials and the availability of the nitrogen proved to be very high. It would seem therefore that activated sludge should find a ready market as a fertilizer ingredient.

**A Proposed Method for the Profitable Utilization of Waste Sulphite Liquor.** HERMAN V. TARTAR, *J. Ind. and Eng. Chem.*, March 1916, pp. 226-8 The liquor is treated with enough sulphuric acid to replace all of the $SO_2$, and then distilled *in vacuo* at a temperature not above 85° C., the $SO_2$ being caught in milk of lime. The last trace of $SO_2$ is oxidized with permanganate, since $SO_2$ is an antiferment and must therefore be all removed. The liquor is now neutralized with lime, and after cooling drawn off from the settled calcium sulphate. Brewers' yeast is added and after the fermentation is complete the alcohol is distilled off. The effluent is non-toxic to fish.

**Contributions to the Knowledge of Adsorption.** V. KUBELKA. *Collegium*, 1915, 389-408. Adsorption is assigned great importance, both in the chemical and the physical theories of tannage. It is defined as change in concentration effected by contact of colloidal or true solutions with substances of greatly developed surface. Most of our knowledge of the subject is derived from the study of reversible adsorption. The amount of the adsorbed substance depends upon the concentration of the solution at the moment of equilibrium; expressed by $a = \beta \cdot c^{1/p}$ where $\beta$ and $1/p$ are constants, $a$ the amount of substance fixed by the unit surface of the adsorbent and $c$ the equilibrium concentration of solution. The determination of $a$ involving surface measurement is very inconvenient and it is usually sufficient to assume that the ratio between surface and mass of the adsorbent is constant. Then $\frac{x}{m} = \beta \cdot c^{1/p}$, where $x$ is the amount of substance withdrawn from solution and $m$ the weight of adsorbent. Most authorities assume the cause of adsorption to be alterations of the bounding surface effected by the dissolved substance. The complicated contact surface, solid-liquid, is the most important in adsorption. The author's research is upon the adsorption of aliphatic acids by hide.

Freiberg unchromed hide powder, containing 12.5 per cent. $H_2O$ was used. It was proved experimentally that the slight acidity of the hide was without influence. The regular research process consisted in shaking 5-6 grams weighed hide powder in a stoppered flask with 100 cc. of the acid solution, either by hand or machinery in lengthy experiments. The

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liquor was then filtered, rejecting the first 30 cc. Room temperature constant, 19°-21°. Barium hydroxide (N/30–N/50) used for titration, phenolphthalein. Pure acids from Kahlbaum were used as material.

I. *Adsorption Equilibrium.*—Schroeder showed that by action of benzoic acid (0.0273 N) upon hide powder, a reversible equilibrium resulted, attainable from either direction, or that the amount of acid at a given concentration taken up by the hide may again be leached out by water, whereby the amount remaining in the hide is in ratio to the concentration according to the exponent of adsorption. The author experimented with formic, acetic, propionic and butyric acids, following Freundlich's method with charcoal. To equal amounts of hide powder were added (1) 50 cc. of acid, concentration $c$; (2) 100 cc. acid, concentration $c/2$; after shaking until equilibrium was established, 50 cc. $H_2O$ were added and shaken an equal time. The concentration was then determined in both experiments. For each acid the reversibility was tested for the approximate limit concentrations of 0.05 and 1.0 gram equivalent per liter. In the double records given below, the first line gives the result on shaking with 100 cc. of a given initial strength (*e. g.*, 0.5394 for formic acid); the second on shaking with 50 cc. of double that strength (here 1.0788), then adding 50 cc. $H_2O$ and again shaking.

| Acid and initial concentr. | $m$ = gms. hide | $c$ = equilibr. conc. | Acid and initial concentr. | $m$ = gms. hide | $c$ = equilibr. conc. |
|---|---|---|---|---|---|
| HCOOH | 4.9784 | 0.5048 | $C_2H_5COOH$ | 5.4091 | 0.4370 |
| 1.0788 | 4.9781 | 0.5042 | 0.9339 | 5.4100 | 0.4377 |
| 0.0592 | 6.2369 | 0.0403 | 0.0372 | 7.2409 | 0.0327 |
| 0.1184 | 6.2364 | 0.0407 | 0.0744 | 7.2415 | 0.0321 |
| $CH_3COOH$ | 5.9009 | 0.5125 | $C_3H_7COOH$ | 4.6357 | 0.4555 |
| 1.0821 | 5.8969 | 0.5131 | 0.9548 | 4.6349 | 0.4564 |
| 0.0634 | 5.2409 | 0.0560 | 0.0564 | 6.8987 | 0.0487 |
| 0.1268 | 5.2412 | 0.0560 | 0.1128 | 6.8994 | 0.0492 |

These results show that the action of the four acids upon hide powder is limited to completely reversible changes.

II. *Velocity of Adsorption.*—Most observers have found that equilibrium is attained very quickly, over 90 per cent. of the change being effected in a few minutes. In the case of textile fibers, however, several days are necessary. The following tables show the author's experiments for velocity upon the four acids; $m$ = grams hide powder; $\gamma$ = initial concentration (milligrams to 1 cc.); $c$ = milligrams adsorbed by 1 gram hide at the instant of equilibrium; $\xi$ = milligrams absorbed by 1 gram hide in the given time. The author's figures for formic acid are given entire. It is seen that equilibrium of adsorption is already reached in the first quarter of an hour. Similar agreements were obtained with the other acids.

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| Time | γ = 0.0502 m | γ = 0.0502 c | γ = 1.1737 m | γ = 1.1737 c |
|---|---|---|---|---|
| 15 minutes | 6.2369 | 0.0403 | 5.0952 | 1.1222 |
| ½ hour | 6.2365 | 0.0410 | 5.0951 | 1.1234 |
| 1 hour | 6.2366 | 0.0408 | 5.0948 | 1.1236 |
| 2 hours | 6.2370 | 0.0403 | 5.0951 | 1.1224 |
| 3 hours | 6.2366 | 0.0403 | 5.0952 | 1.1228 |
| 4 hours | 6.2368 | 0.0403 | 5.0951 | 1.1236 |
| 6 hours | 6.2372 | 0.0403 | 5.0951 | 1.1236 |

Since it was found that further contact up to 6 hours effected no change, 3 hours was taken as the normal duration for shaking. No experiments could be made upon the intensity of shaking, since very moderate agitation quickly established equilibrium.

*Influence of Concentration upon the Velocity of Adsorption.*—The experiments were carried out: (1) for equilibrium, 3 hours action, 70 revolutions per minute; (2) for time experiment, the measured acid was poured upon the hide powder in the flask and the whole uniformly shaken for the prescribed time by hand. The mass was then quickly exhausted on a Witt's plate or centrifuged, just one minute. Experiments were made with various concentrations during equal times. The last column of Tables VII-IX states what percentage of the total change had taken place in the given time.

TABLE VI.—Acetic Acid, 3 Hours Shaking (Equilibrium).

| $m$ | $\gamma$ | $c$ | $\frac{x}{m}$ |
|---|---|---|---|
| 4.9252 | 1.0737 | 1.0345 | 0.796 |
| 5.1316 | 0.7247 | 0.6934 | 0.606 |
| 4.7163 | 0.5396 | 0.5173 | 0.472 |
| 5.5906 | 0.3195 | 0.3012 | 0.328 |
| 5.5370 | 0.1540 | 0.1414 | 0.225 |
| 5.2409 | 0.0633 | 0.0561 | 0.140 |

TABLE VII.—Acetic Acid, 1 Minute.

| $m$ | $\gamma$ | $c$ | $\frac{x}{m}$ | $\frac{\xi}{m}$ | $100\,\frac{\xi}{x}$ % |
|---|---|---|---|---|---|
| 5.9112 | 0.0738 | 0.0647 | 0.160 | 0.155 | 96.9 |
| 5.9109 | 0.0977 | 0.0864 | 0.200 | 0.188 | 94.0 |
| 5.9109 | 0.2100 | 0.1946 | 0.288 | 0.261 | 90.0 |
| 5.9106 | 0.4479 | 0.4269 | 0.429 | 0.354 | 82.4 |
| 5.9111 | 0.6600 | 0.6338 | 0.571 | 0.443 | 77.6 |
| 5.9108 | 0.9324 | 0.8983 | 0.733 | 0.575 | 78.2 |
| 5.9114 | 1.3305 | 1.2913 | 0.952 | 0.665 | 69.8 |

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TABLE VIII.—Acetic Acid, ½ Minute.

| $m$ | $\gamma$ | $c$ | $\frac{x}{m}$ | $\frac{\xi}{m}$ | $100\frac{\xi}{x}$ % |
|---|---|---|---|---|---|
| 5.5951 | 0.0658 | 0.0571 | 0.142 | 0.134 | 94.4 |
| 5.5950 | 0.1110 | 0.0987 | 0.200 | 0.207 | — |
| 5.5955 | 0.3167 | 0.2982 | 0.331 | 0.308 | 93.0 |
| 5.5952 | 0.7519 | 0.7248 | 0.619 | 0.483 | 78.3 |
| 5.5954 | 1.0049 | 0.9742 | 0.775 | 0.549 | 70.8 |

TABLE IX.—Acetic Acid, 5 Seconds.

| | | | | | |
|---|---|---|---|---|---|
| 5.5955 | 0.0878 | 0.0792 | 0.162 | 0.134 | 95.1 |
| 5.5953 | 0.1196 | 0.1088 | 0.200 | 0.193 | 96.4 |
| 5.5955 | 0.3036 | 0.2885 | 0.319 | 0.271 | 84.9 |
| 5.5955 | 0.5892 | 0.5675 | 0.517 | 0.388 | 75.1 |
| 5.5951 | 0.8784 | 0.8531 | 0.712 | 0.452 | 62.1 |
| 5.5950 | 1.1857 | 1.1567 | 0.875 | 0.516 | 58.7 |

The results show that in the range of lowest concentrations over 90 per cent. of the total changes are already effected in the first 5 seconds; the higher the concentration, the smaller the fraction of total change during a given time. The time required therefore to establish equilibrium increases with the concentration, while Georgievics found directly opposite results with wool.

The author shows by further experimental data and discussion, that the quantitative proportions at equilibrium may be satisfactorily expressed by the adsorption formula. Also the proportionality of the dissociation constants and the adsorption constants $\beta$ were proven except in the case of formic acid. With this the proportionality ratio was the closer the lower the concentration. W. J.-K.

## PATENTS.

**Process for Treating Hides. U. S. Patent 1,175,495.** John H. Yocum, East Orange, N. J., assignor to the Clarendon Yocum Company. The process involves the use of salt containing 3% of sodium sulphite.

**Helical Tool. U. S. Patent 1,173,155.** Robert F. Whitney, Winchester, Mass. A workroll for hide-working machines, having a set of spiral cutting blades, each of which has a blunt guard-blade close in front of it.

**Method of Tanning. U. S. Patent 1,173,182.** Gieacomo Durio, Turin, Italy. The hides are stationary and heavy liquors are made to flow past them.

**Chrome Sole Leather. U. S. Patent 1, 173,988.** Martin Szamatolski, Bayonne, N. J., assignor to H. B. Smith, N. Y. Chrome leather is impregnated with a mixture of 5 parts resin, 5 parts naphtha and 1 part paraffin oil.

**Electro Tannage. British Patent 21,190.** Electro-Osmose Company, Frankfurt, A. M., Germany.

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Journal of the

# American Leather Chemists Association

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W. K. ALSOP . . . . . Editor and Manager
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## The American Leather Chemists Association

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Robert E. Johnson, % J. B. Ford Co., Wyandotte, Mich.

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## CASSIUS W. NORRIS

The following is a resolution passed by the Council in behalf of the American Leather Chemists' Association:

> WHEREAS, God in His wisdom has taken from us our colleague, Cassius W. Norris, an early member of our Association and one who always had at heart its best interests and strove for its advancement, a faithful worker whose conscientious labors furthered our knowledge, an efficient officer, a man whose sterling integrity won our respect and friendship; be it
>
> *Resolved,* That our Association herewith record its deep sorrow at his loss.

---

## THIRTEENTH ANNUAL MEETING.

The Thirteenth Annual Meeting of the American Leather Chemists Association will be held at Atlantic City, N. J., on Thursday, Friday, and Saturday, June 1st, 2nd, and 3rd. Headquarters will be at the Hotel Marlborough-Blenheim, where a suitable room will be reserved for our meetings. Those planning to be present at that meeting, should apply directly to the hotel management for reservations, AS EARLY AS POSSIBLE. The rates of this hotel are as follows:

European Plan—

1 room, 1 person, $3.00 and $4.00.
1 room and bath, 1 person, $4.00, $5.00 and $6.00.
1 room, 2 persons, $5.00 and $6.00.
1 room and bath, 2 persons, $6.00, $7.00 and $8.00.

American Plan—

1 room, 1 person, $5.00 and $6.00.
1 room and bath, 1 person, $6.00, $7.00 and $8.00.
1 room, 2 persons, $9.00 and $10.00.
1 room and bath, 2 persons, $10.00, $11.00 and $12.00.

All contributions in the way of papers to be read at the Annual Meeting should be in the secretary's hands at the earliest possible moment.

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Details of the program have not been arranged. The subject of disinfection of hides will be discussed, and it is expected that representatives of the Bureau of Animal Industry will be present to explain the work of the Bureau.

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## AN EXTRACTOR FOR "WATER SOLUBLE MATERIAL" OF LEATHER.

*By Charles R. Oberfell.*

No special claim is made for originality in the design of this battery of extractors for determining the Water Soluble Material of leather. It is a modification of the Teas extractor, described in this J., Vol. I, pp. 181-3, and is a simple and efficient piece of apparatus which is susceptible of easy and accurate control.

The tank *A* is filled with distilled water under pressure from a reservoir above it. This water acts as a water jacket around the extractor funnels *B* for controlling the temperature, and as the solvent. The temperature of this water is held constant by the use of a thermometer and thermoregulator. The flow of water onto the leather is regulated by the stopcock *C*. The leather is contained in an Alundum thimble which fits snugly into *B*. The extract is drawn off at *E* and *D* is used to drain *B* at the completion of the operation. The Alundum thimble should be the most porous obtainable and should be impregnated over one-half of its upper length with Bakelite to compel solvent to pass down through the mass of leather and thereby accomplish the most efficient extraction by diffusion.

The weighing of the leather direct into the thimble is very convenient as well as accurate and provides a means of drying the residue after extraction and reweighing for direct determination of the actual leather substance.

When necessary to degrease the leather, before extraction with water, it is readily accomplished by immersing the thimble containing the leather in petrolic ether after which it may be removed directly to the extractor for water solubles. This elim-

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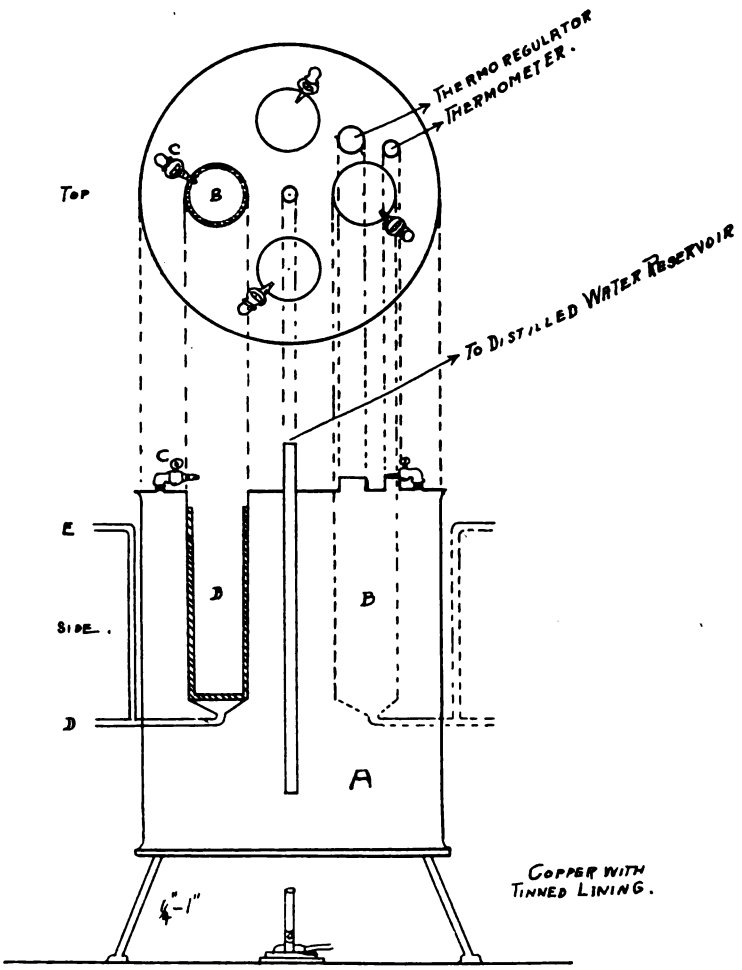
inates transferring the leather from one receptacle to another and increases accuracy as well as saving time.




With this apparatus described four extractions can be run at the same time, but this is not an arbitrary number and a larger or smaller battery would do just as well.

The complete manipulation is as follows: Light the burner under the tank *A* and set the regulator so that the water is heated to 52° C. and held constant at this temperature. Weigh the

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leather into the thimble and place it in *B*. Open cock *C* and place a flask under *E* for collection of the extract. All that is required after this is occasional attention to see that the extraction is proceeding at the required rate. A very clear solution results; one that contains no insolubles.

CHARLES R. OBERFELL,

---

## METHODS DEALING WITH THE ANALYSIS OF MATERIALS IN CONNECTION WITH BEAM-HOUSE PROCEDURE.

*By J. V. R. Evans, Chairman.*

There was no collaborative work done with the Methods Dealing with the Analysis of Materials in Connection with Beam-House Procedure. The methods given are those which have been found to give very good results in this field of work. Methods are included for the analysis of materials used in the beam-house.

The work along this line is far from complete and invites the time and energy of leather chemists in a field which has been neglected but is rich in possibilities.

### LIME.

Analyzed according to the usual methods.

### DETERMINATION OF "AVAILABLE" LIME.

A sample is drawn by breaking off small pieces from a number of lumps of the bulk, coarsely pulverizing them in a mortar, then grinding as fine as possible, and transferring at once to a stoppered bottle for weighing. A portion of this, not exceeding 1 gram, is weighed into a stoppered liter flask, which is filled with hot and well-boiled, distilled water. Allow to stand for some hours with occasional shaking. When cold the flask is filled to the mark with recently boiled distilled water, and again shaken. After it has settled, 25 or 50 cc. are withdrawn with a pipette and titrated with N/10 hydrochloric or sulphuric acid and phenolphthalein. Each cubic centimeter of N/10 acid is equal to 0.0028 gram CaO.

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### Sulphide of Sodium. (Procter's Method.)

Twelve grams of sample is dissolved in water and made up to 1 liter. Sodium is determined by titrating with N/10 hydrochloric or sulphuric acid in presence of methyl-orange which is not sensitive to hydrogen sulphide. Each cubic centimeter of N/10 acid is equal to 2.3 milligrams of Na or 3.9 milligrams of sodium sulphide or 12 milligrams of the crystallized salt.

### Determination of Sulphur as Sulphide. (Procter's Method.)

Fourteen and thirty-five one-hundredth grams of pure crystallized zinc sulphate ($ZnSO_4.7Aq$) is dissolved in water and ammonia is added till the precipitate which is first formed is dissolved, and the whole is made up to a liter. The solution is decinormal and each cubic centimeter equals 1.6 milligrams sulphur or 12 milligrams of the crystallized sulphide of sodium. If 12 grams of sample is made up to 1 liter, and 100 cc. titrated, each cubic centimeter of the N/10 solution will correspond to 1 per cent. of the pure crystallized salt. The standard solution is added with constant stirring to, say 25 cc. of the sodium sulphide solution in a beaker and after each addition a drop is taken from the beaker and placed on a piece of filter paper on a white plate, side by side with one of lead acetate, but not actually touching it, so that the two run together by capillarity. (A somewhat more delicate lead indicator may be made by dissolving lead acetate in solution of sodium tartrate, or tartaric acid made strongly alkaline with sodium hydrate and filtering.) So long as any unprecipitated sulphide is present, a black or brown ring is formed where the two rings come in contact. Care must be taken that the lead solution does not reach the precipitated zinc sulphide, which is always blackened by it. It is best to make a rough determination, adding, say, 2 cc. of standard solution at a time; and having in this way determined the approximate quantity required, nearly the full amount may be added at once.

The zinc process may be employed for the determination of sulphur in other alkaline sulphides, but where polysulphides are present a yellow zinc sulphide is formed, probably a polysulphide, and the lead indicator gives an orange instead of a black ring.

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As a consequence the whole of the sulphur is not determined, but only that corresponding to the normal sulphide.

### Analysis of Arsenic Sulphide.

The sample must be very finely pulverized in an agate mortar. Non-volatile impurities are determined by igniting a small quantity, not exceeding 1 gram, in a porcelain crucible over a good Bunsen burner and weighing the residue.

Both sulphides of arsenic are soluble in cold caustic soda or potash solutions. One gram finely powdered sample is digested for some hours with 50 cc. of 10 per cent. caustic soda solution with frequent shaking, and made up to 100 cc. with water and filtered. The filter is well washed, ignited and the impurities weighed.

The arsenic and sulphur are determined according to the usual gravimetric methods.

### Total Lime.

Shake sample well. Fifty cc. are evaporated to dryness, ignited to destroy organic matter, redissolved in hydrochloric acid and filtered. Add ammonium chloride and then ammonia in slight excess and precipitate with ammonium oxalate and bring to a boil. Filter, wash well with hot water, puncture hole in bottom of filter and wash all of precipitate into an Erlenmeyer flask. Wash filter with 20 cc. of hot 1-1 sulphuric acid, bring contents of flask to 70° C. and titrate with N/10 potassium permanganate. One cc. N/10 potassium permanganate = 0.0028 CaO.

### Lime in Solution.

Determined the same as total lime, only using 10 cc. of the clearly filtered liquor.

### Total Alkalinity.

Pipette 25 cc. of clear filtered liquor into a porcelain dish and titrate with N/10 acid using phenolphthalein as indicator.

### Free Ammonia.

Prepare a bell jar with a base plate and secure two dishes that will fit inside. Place one on top of the other, supporting the upper one by means of a triangle. In the lower dish place 100 cc.

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of the lime liquor and in the upper 25 cc. of N/2 sulphuric acid. Let stand for 24 to 48 hours, remove the acid dish and determine the amount of acid neutralized by the free ammonia.

### Total Nitrogen.

Fifty cc. of the clear filtered liquor is made slightly acid with sulphuric acid and then concentrated in a 500 cc. Kjeldahl flask. Fifteen to 20 concentrated sulphuric acid and 10 grams powdered potassium sulphate are then added, then digested until colorless. The ammonia is then distilled off into standard acid and the excess of acid is measured with standard alkali.

### Hide Substance in Lime Liquors. (Stiasny's Method.)

Place 50 cc. of the filtered liquor in a beaker and add 100 cc. of distilled water. Neutralize with 10 per cent. acetic acid, using phenolphthalein as indicator. Then N/10 iodine is added in slight excess. The liquor is then titrated with N/10 NaOH until again reddened. Ten cc. of neutral 40 per cent. formaldehyde is added and the titration continued with N/10 NaOH until again reddened. If the formaldehyde is not neutral it may be shaken with barium carbonate and filtered. The number of cubic centimeters used in the last titration is due to the amino acids neutralized.

### Sulphides.

A N/10 solution of zinc sulphate is prepared by dissolving 14.38 grams of crystallized salt in water and adding ammonium hydroxide until the precipitate which forms is just dissolved and then adding 50 grams ammonium chloride and making the volume up to 1 liter. Twenty-five cc. of the clear filtered liquor is titrated with this solution using 0.2 per cent. solution of sodium nitroprusside on a spot plate. A drop of the solution is removed from time to time as the titration proceeds and added to the indicator. When a coloration no longer appears the reaction is complete.

### Soaks.

Substances to be determined here are dissolved organic matter and mineral salts that were used in curing the hides. The amount of the dissolved organic matter can be determined by kjeldahling

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and the same tests applied as under lime liquors. The mineral salts used in curing the hides may be tested for both in the hides themselves and also in the soaks and the usual tests applied.

The methods adopted by the I. A. L. T. C. Committee in 1912 cover the field thoroughly. Also the committee report by Mr. Oberfell given in this JOURNAL for May, 1915. Mr. J. Helfrich gives very useful data in his paper on the "Chemical Control of the Beam-House," this JOURNAL, August, 1915.

In regard to the method for the estimation of sulphide, McCandish and Wilson (this JOURNAL, 1914, pp. 203-7) make the point that in making up the zinc sulphate solution, the solution is to be of a definite concentration when ammonia is added. Hugh Garner Bennett (*Collegium*, 1915, pp. 258-66, 313-22, and 329-35; this JOURNAL, 1915, pp. 98-130) offers suggestions and criticisms of the above methods reported. His method making up the zinc sulphate solution for sulphide determination is as follows:

Fifty grams ammonium chloride and 14.35 grams of $ZnSO_4$, $7H_2O$ are both dissolved completely in about 500 cc. distilled water in a graduated liter flask, and 25 cc. concentrated ammonia (SG.880) are then added. No precipitate is obtained. The solution is made up to mark at 15° C.

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## TANNERS' INSTITUTE INSPECTION TOUR.

(Condensed from Bulletin No. 29.)

The fifth annual tour of students and instructors took place April 3d to 7th, the party arriving in Boston at 7 A. M. on the 3d. On that day the plant of Beggs & Cobb at Winchester and the shops of the Whitney Machine Co. were visited. April 4th was spent at the works of the A. C. Lawrence Co., Peabody. April 5th was also spent at Peabody, the morning at the plant of the Turner Tanning Machinery Co. and the afternoon at the calfskin tannery of the Hunt-Rankin Co., and at the hair plant of the Illinois Leather Co. The morning of the 6th was devoted to the goatskin tannery of the H. W. Moore Co., and the afternoon to sight-seeing in Boston. On Friday, the 7th, the party were the guests of the Graton & Knight Co. at Worcester.

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## REPORT OF COMMITTEE ON SULPHONATED OIL ANALYSIS.

*By C. R. Oberfell, Chairman.*

Recent criticisms, both in our JOURNAL and at the Annual Meeting, of our Provisional Methods for the analysis of Sulphonated Oils have had a tendency to lead to the conclusion that they are largely defective and inadequate to supply the necessary data concerning this type of oil. As a result the work for the Committee this year was to consider anew the whole subject and especially in the light of additional knowledge and information developed as a result of experience in the manufacture and use of these oils.

Dr. Gebhardt Bumcke published in the November 1915 issue of our JOURNAL a criticism of the Provisional Methods and made definite suggestions as to preferable methods and means of valuation. This gave your Committee a good basis for starting its work and as a result of a conference of the Chairman with Dr. Bumcke and Boehringer a general letter was sent to the members which outlined the two views of the situation and called for a general discussion with recommendations. The chief criticism of the Provisional Methods centered in the determination of the total fatty oil because it is obtained as the difference between 100 per cent. and the sum of moisture, ash and non-saponifiable. The contention of error in this is stated by Bumcke in the paper above referred to as follows: "The ash will contain only the salts of fixed alkalies while ammonia and its salts are entirely lost, so is glycerin which is usually present to the amount of ½ to 1 per cent. Sulphates of heavy metals are more or less reduced to oxides in the ash and the loss of $SO_3$ though small, will also be calculated as total fatty matter. Any loss of unsaponifiable which easily occurs when very light mineral oils are present would also be calculated to the good of the amount of fatty oil. For correct results the direct determination of the total fatty oil is unavoidable."

It is conceded by the Chairman that the practice of neutralizing with ammonia has resulted in the error in the total fatty oil when estimated by difference. This can be improved by determining the ammonia separately, and adding the amount found to the total fixed ash.

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The other appreciable error is due to glycerin and resolves itself into a question of which is preferred; total fatty oil as the original glyceride (found by the Provisional Method), or total fatty acids (found by the direct method). It is certain that when cod oil, neatsfoot oil, corn oil, etc. are bought it is not on a basis of total fatty acids, but always in combination with glycerin which constitutes the neutral oil. Consequently the Provisional Method gives results comparable to the original glyceride used in its manufacture. An additional argument against the direct determination of the total fatty oil lies in the fact that the method itself is in error. This method depends on the liberation of the fatty material from combination with alkalies and sulphuric acid by boiling reflux with hydrochloric acid. This object is only partially accomplished with some oils. The chairman has found that the liberation from the alkalies is complete, but is not complete from the sulphuric acid. This was demonstrated qualitatively by ashing the separated fats with a fixed alkali and testing the result for sulphates. They are frequently present. In other words, the boiling with hydrochloric acid does not decompose all of the sulpho-fatty acids.

The other errors mentioned which are due to the indirect method, namely reduction of sulphates to sulphides and oxides and presence of volatile mineral products is of scientific interest but may be dismissed as having no practical bearing. In the analysis of a product of such indefinite composition as a sulphonated oil it is hardly to be expected that every possible error can be eliminated.

The general letter to the Committee was in part as follows:

"Two members of this Committee, Drs. Bumcke and Boehringer, who were in Philadelphia recently, met in my office and discussed this question of methods for the analysis of sulphonated oils. I might say that these gentlemen are both interested in the manufacture of sulphonated oils although connected with different firms.

"As you know from the JOURNAL, Dr. Bumcke has proposed certain methods which are essentially, he informs me, those employed in the German Government laboratories. They were designed primarily for sulphonated castor oil products, and it should be remembered that the sulphonated oils as sold to the leather trade to-day are made from a great many kinds of oils, animal, marine and vegetable. However, I understand Dr. Bumcke has so altered the methods that as they are now presented they are applicable to the analysis of all sulphonated oils used for leather.

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"It is hardly worth while to review the development of the present Provisional Methods, so that the discussion will relate largely to the applicability of the methods proposed by Dr. Bumcke and the desirability of incorporating them as official methods should they prove adequate and susceptible of yielding concordant results in the hands of various operators.

"The proposed methods will estimate the following items:

| A | B (Supplementary to A) |
|---|---|
| 1. Water | 1. Neutral (unaltered) oil |
| 2. Total fatty material | 2. Non-saponifiable |
| 3. Ammonia | 3. Oxidized fatty acids |
| 4. Fixed alkali (ash) | 4. $SO_3$ in salts |
| 5. Total $SO_3$—100 per cent. | 5. $SO_3$ organically combined from which sulpho-fatty acids are calculated |
| | 6. Free fatty acids |

"Dr. Bumcke is of the opinion that all of the items under A and B are necessary because he thinks that without the full data thus obtainable one is unable to judge properly of the value of any oil for certain work. Also these complete data give a very definite idea of the composition of the oil from which one could say whether the oil was properly manufactured or not. I have tried to put correctly in a few words Dr. Bumcke's ideas as I gathered them from his conversation.

"On the other hand, I do not fully agree with Dr. Bumcke, and Dr. Boehringer supports me in this, because our knowledge of the effect of all or part of the items under B is meager and is not linked up closely enough with practical tests to enable anyone at this time to use the data obtainable by these tests in placing a final value on the oil. Methods so accurate that all have confidence in them for buying and selling are most urgently required.

"Unless we can say exactly the effect of a certain amount of oxidized fatty acids, or of free fatty acids, why should the American Leather Chemists' Association adopt such methods, however accurately the method may determine the constituent named? Would it not be better simply to define methods whereby the manufacturer and user can get together on an equitable basis?"

The members of the Committee comment as follows:

JOHN H. YOCUM: "Replying to your favor of March 2nd regarding the work which you are doing on the sulphonated oil committee, would state that the German method of analyzing oil is probably all right, but I would like to see the man who is going to pay for the analysis.

"Under item A, you mention water, total fatty material, ammonia, fixed alkali, and total $SO_3$. These will not add up to

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100 in that there will be some other ash present which will not come under the heading of fixed alkali, and no consideration of unsaponifiables is taken; and besides, the sulphonated fats, which includes the total $SO_3$, will come in under total fatty material.

"In the items under B, the only ones of importance are unsaponifiables and neutral oils. I fully agree with you that our knowledge of the determination of most of the items under B is so limited, that the analysis would be worthless, and that we should get simple methods which are sufficiently accurate, so that some valuation of the oil can be obtained.

"In fact, I do not think the present methods are very obsolete, with the exception that they do not take care of ammonia oils. A complete analysis including the eleven items specified under A and B, would be Greek to all tanners and to most chemists, and I do not think, with the exception of a few items which are already taken care of, that it would give anyone any considerable amount of information.

"The fact of the matter is that sulphonated oils cannot be judged by an analysis in the same way as straight oil, extract, or most of the other materials which are used in the tannery. The oil which will do the work is the one the tanner will buy, and outside of moisture and unsaponifiable, he does not care much about the analysis, although he would like to have some idea of the degree of sulphonation."

A. W. HOPPENSTEDT: "For defining methods for the buying and selling of sulphonated oils I am of the opinion that at present the following determinations would be all that are required:

Water.
Ash.
Total Fatty Matter.
Unsaponifiable Fatty Matter.
Presence of Ammonia (Qualitative).

"These determinations are all very simple and can be easily and accurately made and they therefore would form an equitable basis for the buying and selling of these oils. The total fatty matter is the one that forms the main basis and the unsaponifiable fatty matter shows up the character of the same. The total fatty matter without a determination of the unsaponifiable fatty

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matter would not mean very much. The addition of any other determination besides the ones given above could also be put on any report when desirable, but for buying and selling the ones given should suffice and would constitute items that can be accurately determined and to which there should therefore be no opposition."

ADOLPH SCHUBERT: "I have your letter of March 3rd regarding the analysis of sulphonated oils, and in reply would say that the system proposed is entirely too complex, especially when our knowledge of the items under B is so vague, and the methods of analysis are not sufficiently accurate. In my opinion the analysis should be reported as follows:

1. Water.
2. Ash.
3. Ammonia.
4. Nonsaponifiable Oils.
5. Unsulphonated Oils (not including Nonsaponifiable Oils.)
6. Sulphonated Oils (by difference)

Total 100%

"This analysis would give all the information desired by a user of sulphonated oils. For factory control work it would be necessary to determine the $SO_3$ organically and inorganically combined, but I believe that we are not establishing a factory control method but rather one which is of use and value to the user of the oil, and to him the above mentioned analysis would give all the information necessary for controlling the purchases and use of the oil."

RUDOLPH BOEHRINGER: "In my opinion, the items under A should be modified to some extent; my main objection to A as it stands in your letter is that you have not taken into consideration the "unsaponifiable." Mineral oils are very often used in mixtures with the sulphonated oils and very often those mixtures are the only means to meet competition in low priced oils. While I admit that our knowledge regarding small amounts of mineral oils mixed with sulphonated oils in its use on leather are rather meager, the buyer of the oil should know what he is purchasing.

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"The determination of the total $SO_3$ alone is misleading as the amount of inorganic sulphates may be varied very considerably, according to the methods of manufacture. A product sulphonated with a small percentage of $H_2SO_4$, not properly washed or not washed at all, may show a larger amount of total $SO_3$, than another one sulphonated with a higher percentage of $H_2SO_4$ and properly washed. This fact brings me to the conclusion that we must either advise the determination of $SO_3$ organically combined and $SO_3$ in salts or not at all.

"Determination of ammonia and fixed alkali is in my mind rather problematical, although I admit its determination is of no harm.

"For some time to come total fatty material and its percentage of unsaponifiable will be in my opinion the basis for buying and selling and not the percentage of $H_2O$ which is so unfair to the buyer.

"I am of the opinion that we are not justified in recommending any other determinations as standards until it can be proven what actions neutral oils, free fatty acids, sulpho-fatty acids and oxidized fatty acids play in their uses on leather."

GEBHARDT BUMCKE: "I strongly recommend to replace the two items $B_4$ and $B_5$ for the item $A_5$, as I consider it of the utmost importance not to omit the test for '$SO_3$ in salts' as the 'total $SO_3$' alone does not admit a sufficient foundation to judge whether one oil is higher sulphonated than another. The amount of '$SO_3$ in sulpho-fatty acids' alone gives an estimate how highly an oil is sulphonated.

"From my practical experience with tanners I can tell you that I have heard that our products were too highly sulphonated for one purpose while they were not highly enough sulphonated for another. From this I make the conclusion that there is an absolute necessity to tell in figures how highly an oil is sulphonated and this figure is given by the amount of '$SO_3$ in sulpho-fatty acids' or the amount of sulpho-fatty acids proper by multiplying the aforesaid figure by a factor (4.75).

"I further recommend to add under B a test describing the behavior of an oil when 1–2 cc. of it are poured into a test tube full of distilled water, whether it dissolves immediately, slowly

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or only after shaking, whether it makes an emulsion, a milky, an opalescent or a clear solution and what this does after adding a few drops of ammonia, whether it stays cloudy, clears up a little or becomes a perfectly bright solution. This is only a qualitative test and a rather crude one but it is quick and admits some conclusion as to the usefulness of an oil for one purpose or another.

"I further want to add that for practical use I consider the items B1 and B2 more important than those under A3 and A4.

"The amount of free fatty acids B6 seems rather immaterial to me, as sulphonated oils, like acid fat liquors, are used when tanning on the acid side and the amount of alkali necessary to clear up a solution of a sulphonated oil is more governed by the amount of sulpho-fatty acids than that of free fatty acids, an oil with high percentage of sulpho-fatty acids needs little or no alkali to make a clear solution in water, while an oil with low percentage of sulpho-fatty acids will not clear up even when all free fatty acids are neutralized."

These opinions would indicate that the Committee is not in favor of drawing methods for an elaborate analysis whereby an attempt could be made to value the oil, but is in favor of methods whereby the manufacturer and consumer can meet on an equitable basis.

A scheme such as the following would meet the ideas of the Committee

Water.
Ammonia.
Ash.
Nonsaponifiable.
Total Fatty Oil (by difference)
100%

Regarding the determination of the neutral or unaltered oil in the total fatty oil, the facts are that a real method does not exist. The present proposals are unsatisfactory to operate and inaccurate as well. No new ideas have been advanced for this determination.

The chairman recommends the following:

Ammonia ($NH_3$).—Extract four times with 10 cc. (1 : 5) sul-

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phuric acid in a separatory funnel, 10 grams oil dissolved in 150 cc. ethyl ether. The acid wash water is obtained in a flask from which it is distilled, after adding excess of a fixed alkali, into 100 cc. N/10 acid. The amount of ammonia is obtained by titration.

Total Fatty Oil.—The total fatty oil shall be the difference between 100 per cent. and the sum of moisture, ash, ammonia and nonsaponifiable.

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## THE LEATHER INDUSTRY OF THE PHILIPPINE ISLANDS.[1]

*By Vincente Q. Gana.*

(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

There exists in the Philippine Islands a considerable, but very primitive, tanning industry. The methods now in use have not undergone substantial modification since they were introduced by the Chinese, probably several centuries ago. Consequently the leather produced is inferior in quality, especially so since tanning in a tropical country involves difficulties not encountered elsewhere. There is no obstacle to a great expansion of this industry. The leather market is good, and additional supplies of the necessary materials can be had in considerable quantities and at fairly reasonable prices. Therefore, in order to stimulate the industry, an extensive study of the existing industry and some practical experiments using improved methods have been carried on.

Data regarding the leather industry furnished by the provincial treasurers are given in Table I.

Although doubtless lacking great accuracy, the statistics show that the tanning industry produces leather to the value of from 1,500,000 to 1,800,000 pesos[2] per annum. On the whole, the figures regarding production are believed to be too low.

### The Local Leather Market.

There is a large and increasing local demand for leather and leather goods which is met almost entirely by importation. Table II shows the Philippine customs invoice value of imports of leather and manufactures thereof for several years.

[1] *The Philippine Journal of Science* (*A*), Vol. 10, No. 6, November, 1915.

[2] One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

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TABLE I.—NUMBER AND OUTPUT OF TANNERIES OF THE PHILIPPINE ISLANDS.

| Locality | Tanneries. | Tanned hides produced. | Locality | Tanneries. | Tanned hides produced. |
|---|---|---|---|---|---|
| Manila | 8 | 39,050 | Tayabas | 2 | 250 |
| Bulacan | 11 | 36,000 | Batagas | 19 | 220 |
| Iloilo | 3 | 5,929 | Zamboanga | 1 | 216 |
| Cebu | 4 | 4,401 | Nueva Ecija | 4 | 164 |
| Pangasinan | 11 | 2,600 | Sorsogon | 1 | 120 |
| Albay | 4 | 1,320 | Antique | 2 | 70 |
| Ilocos Sur | 37 | 1,130 | Cavite | 4 | 65 |
| Ilocos Norte | 13 | 1,114 | Cagayan | 17 | 54 |
| Ambos Camarines | 3 | 270 | Capiz | 22 | 22 |
| Rizal | 1 | 250 | Total | 167 | 93,245 |

TABLE II.—INVOICE VALUE OF IMPORTS OF LEATHER.

| Year | Pesos | Year | Pesos |
|---|---|---|---|
| 1903 | 1,373,572 | 1909 | 988,276 |
| 1904 | 985,070 | 1910 | 1,520,926 |
| 1905 | 986,334 | 1911 | 1,988,382 |
| 1906 | 922,440 | 1912 | 2,051,614 |
| 1907 | 958,268 | 1913 | 2,380,246 |
| 1908 | 1,343,924 | | |

The actual value of these goods is unquestionably several times larger than the invoice value given in the table. A gradual increase has occurred in almost every item included in these figures. Most notable, however, is the increase in the importation of boots and shoes. The introduction of European customs of dress may safely be expected to maintain or accelerate this rate of increase for several years. Table III gives the classification of the leather and manufactures thereof imported during the years 1912 and 1913, as shown by the annual reports of the Collector of Customs. It will be noted that the item boots and shoes constitutes nearly 60 per cent. of the total.

In recent years a number of boot and shoe factories have begun to operate in Manila and they are still expanding. As they consume imported sole and upper leather exclusively, the demand for satisfactory grades of these goods is likely to increase very markedly. It is to these classes of leather that the prospective tanner in the Philippines should devote his first and main attention.

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TABLE III.—Classification and Value of Philippine Imports of Leather and Manufactures Thereof for the Fiscal Years 1912 and 1913.

| | 1912 Pesos | 1913 Pesos |
|---|---|---|
| Boots and shoes | 1,173,904 | 1,390,864 |
| Sole leather | 102,524 | 200,016 |
| Upper leather | 109,886 | 256,534 |
| All other | 519,920 | 253,758 |
| Belting | 65,662 | 59,862 |
| Harness and saddles | 79,718 | 163,594 |
| Pocketbooks, purses, wallets, and hand bags | | 55,618 |
| Total | 2,051,614 | 2,380,246 |

In addition to the industry just mentioned, which uses imported leather and which is conducted by Europeans and Americans, there is an even larger leather-working business among the Filipinos and Chinese. It is carried on in small shops or as a household industry. Its products include cheap shoes, sandals, harness, saddles, bags, etc., made almost exclusively of leather tanned in the Islands. The improvement of domestic leather would, of course, be of great advantage to these industries.

The present prices of staple leathers on the local market are approximately as follows:

TABLE IV.—Prices of Staple Leathers on the Manila Market.

| Article | Per piece | Per kilogram |
|---|---|---|
| | Pesos | Pesos |
| Domestic, tanned, native cattle hides | 13-20 | †1.40-1.80 |
| Domestic, tanned, Australian cattle hides | 16-24 | †1.60-1.90 |
| Imported sole leather | †40-50 | 2.00 |

†Calculated from actual market prices and the average weight of hides.

Quality considered, native leather commands a much better price per kilogram than imported. This arises from the Filipino custom of buying leather by area rather than weight. The loss to the Filipino tanner in producing undertanned leather is very apparent in the prices per piece. There is no exportation of leather or leather goods from the Philippines.

## Raw Hide Supply.

In spite of the inroads which rinderpest has made upon the cattle-raising industry of the Philippines and of the strict limita-

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tions placed in recent years on the importation of animals from abroad, with the consequent shortage on the local market, very many hides and skins go to waste each year.

There has been difficulty in getting reliable information about the supply of hides and skins from domestically slaughtered animals, but from figures of the Bureau of Agriculture it appears that 11,133 sheep, 69,851 goats, 1,019 horses, 36,935 cattle, and 17,890 carabaos were slaughtered in the Philippines during the calendar year 1913. These animals would furnish roughly 90,000 skins and 56,000 heavy hides. The number of available raw hides, according to the reports of the treasurers of the several provinces mentioned in Table I, is 54,057.

Hides and skins are bought and sold by the piece. At market centers salted hides of Australian cattle average about 16 pesos and of native or Chinese cattle about 10 pesos. This amounts to about 65 centavos per kilogram for the former and 60 centavos per kilogram for the latter. However, in many provinces cattle hides can be bought as low as 1 peso per piece and average less than 5 pesos. They are frequently not removed from the animals. There is a small production of dried hides which are exported to Hongkong and British East Indies for the manufacture of glue. Table V gives the value of such exports.

TABLE V.—EXPORTS OF DRIED HIDES FROM THE PHILIPPINE ISLANDS TO HONGKONG AND BRITISH EAST INDIES.

| Year | Pesos | Year | Pesos |
|---|---|---|---|
| 1907 | 30,336 | 1911 | 22,626 |
| 1908 | 25,710 | 1912 | 22,626 |
| 1909 | 27,920 | 1913 | 29,492 |
| 1910 | 46,074 | | |

Very little care is exercised in the method of preserving hides for the market. Systematic salting is not in general use, and many hides reach the tanner in a semiputrid condition. The process of salting hides is a very simple one and consists in the even distribution of salt, about 25 kilograms for every hundred kilograms of hides, over the flesh side of the hides in a layer so thick that solid salt always remains. The hides should be stacked in such a way that the draining away of any resulting brine will be prevented. Hides which are salted with reasonable care keep very well, even in this climate.

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In addition to the domestic product, there has been a considerable importation of raw hides and skins into the Philippines during the last four or five years. The imported hides come almost exclusively from China. Table VI gives the figures of the importation of raw hides and skins.

TABLE VI.—VALUE OF IMPORTS OF RAW HIDES INTO THE PHILIPPINE ISLANDS.

| Year | Pesos | Year | Pesos |
|---|---|---|---|
| 1907 | 9,056 | 1911 | 36,210 |
| 1908 | 19,906 | 1912 | 151,222 |
| 1909 | †39,326 | 1913 | 62,428 |
| 1910 | ‡76,772 | | |

† From China. ‡ Mostly from China.

The weights and prices of these imported hides are given in Table VII.

TABLE VII.—WEIGHTS AND MARKET PRICES OF RAW SALTED HIDES IN MANILA.

| Variety | Weight | Price per hide |
|---|---|---|
| | *Kilograms* | *Pesos* |
| Australian cattle hides | 20-25 | 13-16 |
| Chinese cattle hides | 15-21 | 7-12 |
| Carabao hides | 18-35 | 6- 8 |
| Native cattle hides | 15-30 | 5-15 |

## TANNING MATERIALS.

The only tanning materials used in the Philippines are the barks of the various species of mangrove (Rhizophoraceae or mangrove family) and the camanchile tree (*Pithecolobium dulce* Benth.). The former are very plentiful and cheap, selling for about 25 pesos per metric ton. In spite of this fact and in spite of their high tannin content, mangrove barks are not extensively used in the Philippines outside of the city of Manila. This is primarily because of the resulting harshness and dark red color of leather tanned with mangrove alone. However, good light-colored leathers can be produced by combining camanchile and mangrove, as I have demonstrated by experiments which will be discussed later. The mangrove barks have been considerably studied[3] and are widely used in Europe and America. Their use may well be extended in the Philippines.

[3] Bacon and Gana, *This Journal*, Vol. 6, (1911), 124, Williams, R. R., ibid. (1911), 389. The waste wood can be utilized for firewood or for destructive distillation, as shown by experiments now under way.

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Camanchile bark is used almost exclusively by Filipino tanners, who prefer it on account of the light-colored leather it produces. Because of this demand the price of air-dried camanchile bark has risen as high as 10 pesos per 100 kilograms. The tree is widely scattered throughout the Islands, although nowhere systematically or extensively grown. The present annual consumption of bark amounts to about 1,500 tons. Exhaustion of the supply is threatened, as the trees are commonly killed by too extensive stripping of the bark. The bark is brownish gray and rough outside and reddish brown inside. It produces dull but light-colored leather, which reddens on exposure to light. An infusion of it contains a tannin of the catechol class, which gives a green-black precipitate with iron salts, a light brown precipitate with bromine water, and crimson line when in contact with one drop of concentrated sulphuric acid. Upon analysis a representative sample of the bark gave the following results, calculated on water-free material: Total extract, 34.77 per cent.; non-tannin, 9.41 per cent.; tannin, 25.36 per cent.

Camanchile bark infusion soon ferments and decomposes in this climate, resulting in the destruction of tannins, the development of a disagreeable odor, and a thickening of the liquid due to a viscuous gelatinous formation which accumulates and grows on the surface. A few experiments with phenol as a preservative showed that a concentration of 0.01 per cent. does not check the fermentation appreciably, as in a control infusion the tannins were destroyed, the color became a deep wine red—at least three times as intense as the original red orange—a somewhat penetrating smell was given off, and a gelatinous formation and a slimy sediment developed, which made the infusion viscous. After four months the loss of tannin amounted to 15 per cent. of the total tannin content. An infusion containing 0.1 per cent. phenol at the end of the same period showed a practically unaltered tannin content and an acidity equal to 0.0714 gram acetic acid per 100 cubic centimeters. A little fermentation which soon ceased had produced some slimy sedimentation, but had not altered the appearance or odor of the clear supernatant infusion.

Camanchile bark contains irritating principles, which are believed by laborers in the tanneries to indicate roughly the strength

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of infusions. Infection of the eyes, producing weakening of the sight, and irritation and swelling of the lids are attributed to them.

Through the co-operation of Dr. Fred W. Foxworthy, of the College of Forestry at Los Baños, who collected and sent me the material, I was enabled to examine several barks and fruits which have not as yet been used as tanning materials. The results are presented in Table VIII.

Of these tanning materials none seems particularly promising, either on account of the insufficient supply or on account of the low tannin content.

### The Filipino Process of Tanning.

As has been stated previously, the Filipino process of tanning is very primitive and produces a very inferior grade of leather. It was desired to make a study of this process in order to point out its prime defects and to suggest improvements which might be put into effect without materially increasing the investment in equipment or supplies. For this purpose the tanning industry as conducted at Meycauayan, Bulacan, was chosen for study. Meycauayan is one of the largest leather-manufacturing centers in the Philippines, and its methods are fairly representative of those of the Islands as a whole. Eleven tanneries are located there, with an aggregate output of 36,000 pieces per year, consisting almost wholly of cattle hides. These include practically the entire product of the Government slaughterhouse at Sisiman and an almost equal number of imported hides from Hongkong. A few carabao hides are tanned, but the Filipino tanners are not willing to attempt the tanning of these hides except under exceptional circumstances. On account of their thickness they are very hard to tan and they are liable to putrefaction. Therefore they are usually split, and very commonly only the grain side is tanned, the remainder being discarded or used for glue.

The leather produced by the Filipino process is soft and pliable and, in general, is very much undertanned. It is characterized by an unpleasant odor, especially when wet. This leather lacks the firmness and durability desirable in sole leather and, at the same time, is too thick for first-class upper leather.

The salted hides, as received at Meycauayan, are usually in good condition, not showing evidences of decay or having partic-

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TABLE VIII.—ANALYSES OF MISCELLANEOUS TANNING MATERIALS.

| Sample No. | Material | Botanical name | Distribution | Precipitate with ferric salts | Precipitate with bromine water | Color on contact with concentrated sulphuric acid | Moisture % | Tannin % | Nontans % | Character of leather produced |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Cateban bark | *Quercus* sp | Scattered in hilly districts | Blue-Black | Brown | Red brown | 10.2 | 10.9 | 4.2 | Rather hard; hazelnut brown. |
| 2 | Ulayan bark | " | " | " | " | " | 10.2 | 11.0 | 3.9 | Satisfactory texture; hazelnut brown. |
| 3 | Balinghasay bark | *Buchanania arborescens* | Scattered generally | Green-black | " | Deep Brown | 8.7 | 8.2 | 7.6 | Hard and somewhat harsh; dark reddish brown. |
| 4 | Pagsahinging bark | *Canarium villosum* | Common in hilly districts | " | Yellowish brown | Pink | 8.0 | 2.8 | 5.5 | Thin and soft; pale brown. |
| 5 | Calamansanay bark | *Nauclea calycina* | Scattered in hills | " | Brown | Brown | 8.8 | 6.5 | 7.6 | Thin; very dark red. |
| 6 | Ligas bark* | *Semicarpus accuminatissima* | Scattered generally | " | Yellowish brown | Pink | 8.0 | 2.2 | 4.3 | Thick; reddish brown. |
| 7 | Sacat fruit | *Terminalia nitens* | " | " | Light brown | Reddish brown | 8.9 | 19.8 | 16.3 | Thin, smooth grain; dark color. |

* The sap of this tree produces blisters on the skin.

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ularly offensive odors. They are laid in packs of from 17 to 20 and are soaked for about eight hours in water in the bed of a river. They are then removed to lime pits of masonry construction, which are usually placed in a series of from 10 to 20, in the open air without protection from sun or rain. The usual dimensions of a pit are 1.7 meters by 0.9 meter, with a depth of 0.8 meter. A pack of 20 hides is laid in the pit, 25 liters of lime and sufficient water nearly to fill the pit being used for the liming process. The water used is taken either from the river or from shallow surface wells near by.

The method of preparing the lime liquors and laying the hides in the liming pits is as follows: The lime is mixed with water, and the gravel and the coarser particles are removed with a bamboo sieve. A hide is laid in this liquor, folded lengthwise with the hair outside. Other hides are placed on top in the same manner, until the pack is complete. The hides are left in the lime pits for from ten to fifteen days, during which time they are overhauled three or four times. At each overhauling the order of laying is reversed, so that the upper hide in the pack is laid at the bottom, and so on. The exact duration of the liming process is determined by the loosening of the hair and the degree of plumping of the skin. Frequently after the hides have been removed from the lime pits and have been fleshed and dehaired, they are again returned to the lime liquors if the tanner believes more plumping is desirable. The lime liquors are used only once.

The limed hides are taken to the river and depilated, fleshed, and cleaned by scraping the hide with a blunt knife to take out as much lime as possible. They are left in the river under water for a few hours to be freed from lime and are then ready for the tan pits. Except the hair, all the fleshings and scrapings and even parts of the pelt itself go to the refuse basket. All this waste is mixed with the lime and pressed into cakes, dried in the sun, and sold for 9 pesos a picul[4] to glue makers. This return is customarily divided into one half for the tanner and the other half for the laborers.

The tan pits, partly above the surface of the ground, under cover of a large, open shed, are walled up with adobe stone[5]

[4] One picul is equivalent to 63.25 kilograms.
[5] Porous volcanic tuff.

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and ordinary mortar. Each pit measures 1.9 meters by 1 meter with a depth of 1.2 meters and holds 20 native or Chinese cattle hides or 17 Australian hides. For each such pack a tan bark infusion is prepared by placing from 500 to 600 kilograms of chopped camanchile bark in the tan pit and macerating it for three days with about 1,200 liters of a liquid consisting of two thirds fresh water from a surface well and one third old, used tan liquor. A date for making the infusion is so chosen that the dressed hides will be ready for the tan pits on the fourth day. The bark is then removed and used for laying between the hides.

In laying away the pack, the workman places a hide smoothly grain side up, so that about half its surface rests on a layer of bark in the bottom of the pit. Another layer of bark is spread over this surface, and the other half of the hide, which has in the meantime been supported in the hands, is folded along the middle of the back down upon the bark. After another layer of bark has been placed over this hide, the remainder of the pack follows in the same manner, and the whole of the bark infusion is added. The pack is handled and the hides are kneaded with bare feet four times during tannage, usually once on each of the first four days. After each handling the hides are returned to the pit as before. Sometimes a fifth handling and kneading or even a sixth is resorted to when necessary to prevent putrefaction.

The object of kneading is to compress and distort the hide fiber and to hasten the absorption of the tannin. Such is the effect of kneading that the hides are almost half "struck" by the fourth day. They are then laid away in the tan pits for six weeks to complete the tannage. After this, if they are not to be sent to market immediately, they are laid in pits, called *tingalan,* with old, exhausted tan liquor. Sometimes they are left here for years. When required, they are taken to the river, thoroughly washed and cleaned, stretched on sticks, and exposed to direct sunlight. When dry, they are sent directly to the market without further treatment.

### Defects of the Filipino Process.

The process outlined above is very inefficient in many respects.

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In a study of the process the following defects proved to be among the most significant:

1. The putrefaction of the hides during the process with consequent loss of hide substance.
2. Waste in tanning materials.
3. Undertannage of the product.
4. Imperfect drying and finishing.

Of these defects by far the most important is that of putrefaction. During the rainy season this is especially difficult for the tanner to prevent, and it is commonly the custom to shut down the tanneries almost completely during that period. The decay is evidenced by a very disagreeable odor which not only develops in the leather itself, but which also pervades the entire tannery and becomes almost suffocating. Skins in which putrefaction occurs tan on both exterior surfaces, while the interior of the hide liquefies. The pelt commonly splits into grain and flesh sheets. The Filipino tanners attribute the putrefaction to dilute tan liquors, which they believe are caused by the use of barks collected during the rainy season. Usually the putrefaction occurs most markedly during the first days of tannage, and at this stage soft, gray spots, which frequently suppurate, may develop. Such spots do not tan at all, and, of course, the entire skin is ruined thereby. Aside from this ruining of the skins by putrefaction, a less extensive decay prevents proper plumping and swelling of the hides and consequent proper absorption of tannin. For this reason it is almost impossible for Filipino tanners to tan thick hides.

The Filipino tanners endeavor to control this putrefaction by adding large quantities of fresh bark to the tan pits and by more frequent kneading of the hides. This procedure, however, is very ineffective, especially so since the tanner often fails to detect decay until it has proceeded beyond remedy.

The obvious measures to be taken to prevent this difficulty consist simply in greater cleanliness during the entire process. Tan pits, handling floors, and the like should be frequently cleaned and disinfected. Water free from pollution or unusual amounts of mineral matter is also a necessity. The river, on which the tanneries of Meycauayan are located, flows into Manila Bay and is subject to tidal variation. It is, therefore, decidedly brackish

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and falls far short of what is to be desired in a water for this purpose. Table IX presents an analysis of this water.

TABLE IX.—ANALYSIS OF MEYCAUAYAN RIVER WATER.

[Numbers represent parts per million.]

| | |
|---|---|
| Physical characters | brownish yellow with salt taste |
| Reaction | alkaline |
| Total solids | 52,672.0 |
| Appearance on ignition | blackening and evolution of hydrochloric acid. |
| Free or saline ammonia | 0.37 |
| Organic or albuminoid ammonia | 0.68 |
| Oxygen consumed | 50.00 |
| Chlorine | 26,284.4 |
| Equivalent to common salt | 43,313.7 |
| Nitrogen as nitrates | trace |
| Nitrogen as nitrites | nil |
| Silica ($SiO_2$) | 25.6 |
| Oxides of iron and aluminium (practically all Al). | 21.0 |
| Oxide of calcium (CaO) | 809.0 |
| Oxide of magnesium (MgO) | 2,909.3 |
| Sulphuric anhydride ($SO_3$) | 2,706.7 |
| Total hardness: | 8,663.7 |
| Permanent | 8,571.2 |
| Temporary | 92.5 |
| Bicarbonic acid radical ($HCO_3$) | 142.1 |
| Carbonic acid radical ($CO_3$) | nil |
| Free carbon dioxide ($CO_2$) | 4.4 |

Aside from the large amount of mineral matter present, this water is also objectionable on account of the large quantities of putrefying organic matter ordinarily found in it. A loop of water invariably produced liquefaction in serum and gelatin tubes within forty-eight hours' incubation at ordinary temperature.

Table X gives the analysis of a typical sample of water from surface wells in this locality such as are used for making up tan liquors.

Analyses of the liquors used at various stages of the process show very clearly the progress of putrefaction and loss of hide substance. The lime used is made by burning sea shells; it has a total alkalinity equivalent to about 70 per cent. calcium hydroxide. An analysis of a typical lime liquor, after removal of the hides, is shown in Table XI.

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TABLE X.—ANALYSIS OF WATER FROM A SURFACE WELL AT MEYCAUAYAN.

[Numbers represent parts per million.]

| | |
|---|---|
| Physical character | normal |
| Reaction | neutral |
| Total solids | 946.0 |
| Appearance on ignition | evolution of hydrochloric acid |
| Free or saline ammonia | 0.048 |
| Organic or albuminoid ammonia | 0.068 |
| Clorine | 203.6 |
| Nitrogen as nitrates | trace |
| Nitrogen as nitrites | 0.016 |
| Silica ($SiO_2$) | 39.7 |
| Oxides of iron and aluminium (largely Al) | 48.0 |
| Oxides of calcium (CaO) | 165.0 |
| Oxides of magnesium (MgO) | 20.6 |
| Sulphuric anhydride ($SO_3$) | 41.1 |
| Bicarbonic acid radical ($HCO_3$) | 179.2 |
| Free carbon dioxide ($CO_2$) | 13.2 |
| Total hardness: | 486.6 |
| Permanent | 351.0 |
| Temporary | 135.6 |

TABLE XI.—LIME LIQUOR FROM A FILIPINO TANNERY AFTER REMOVAL OF THE HIDES.

| | Grams per 100 cc. |
|---|---|
| Nitrogen as ammonia | 0.0457 |
| Equivalent hide substance | 0.266 |
| Total hide substance | 0.987 |
| Unchanged hide substance | 0.721 |

These figures show that nearly 8 kilograms of dissolved hide substance are lost from each pack of twenty hides weighing approximately 230 kilograms, which is equivalent to about 3.5 per cent. of the weight of the hides.

Fresh lime liquors about 2 days old are almost sterile, but easily become contaminated by the surface drainage. When 1 week old a loopful of lime liquor will liquefy gelatin within six days' incubation at ordinary temperature. The lime liquors invariably have a strong ammoniacal odor after two days in contact with hides.

A piece of green pelt from a tannery, weighing about 2 kilograms after dehairing and fleshing, was kept in 2 per cent. aqueous solution of phenol. On the fourth day the hide substance

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dissolved in the liquid was found to be 2.66 grams, or 0.133 per cent. of the wet pelt. The phenol solution was changed for a fresh one which, after nineteen days, gave but a faint precipitation ring with a tan infusion. This same phenol solution, after four and a half months in contact with the hide, gave a much stronger precipitation ring, which must be due, not to any further decomposition, but probably to the outward diffusion of dissolved hide substance previously developed inside of the pelt. There cannot have been any putrefaction in the phenol solution, as demonstrated by pieces of the same pelts which remained unaltered in acid and alkaline bouillon tubes for nearly six months. This soluble hide substance is the product of bacterial activity in the pelt.[6]

Pelt which had been limed, fleshed, and dehaired by the usual process of the Filipino tanner, after being kept for one month in 2 per cent. phenol solution, gave on analysis the results included in Table XII.

TABLE XII.—ANALYSIS OF LIMED, FLESHED, AND DEHAIRED PELT.

| Substance | Calculated on the basis of green pelt | Calculated to a water-free basis |
|---|---|---|
| | Per cent. | Per cent. |
| Water | 71.50 | ..... |
| Nitrogen | 4.23 | 17.3 |
| Equivalent hide substance | 27.70 | 97.2 |
| Lime, etc. | 0.80 | 2.8 |

The liquefying bacterial conditions of the tannery liquors have been determined by means of serum and gelatin media tubes. These tubes were inoculated with one loopful of the tannery liquor and incubated at ordinary temperature—about 30° C. The time period required for the liquefaction of the media is noted in Table XIII.

The data demonstrate that the tan liquors of the Filipino process generally contain abundant putrefying or liquefying bacteria. Even in the case of pelts that had been washed in 0.5 per cent. phenol baths, liquefaction ensued within forty-eight hours when immersed in such liquors. The smell of the leather and tan liquors is due to this putrefaction.

[6] Brunton and MacFadyen, *Proc. Roy. Soc. London* (1890), 46, 542-53.

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TABLE XIII.—LIQUEFACTION OF THE MEDIA DUE TO LIQUEFYING BACTERIA AT A FILIPINO TANNERY.

| Description of sample | Days to liquefy with one loopful of sample | |
|---|---|---|
| | Serum | Gelatin |
| River water used for washing hides | 2 | .. |
| Do | .. | 2 |
| Do | .. | 2 |
| Lime liquor 2 days old | 7 | .. |
| Do | .. | 20 |
| Lime liquor 1 week old | .. | 6 |
| Native tan liquor 1 month old | 2 | .. |
| Native tan liquor | .. | 2 |
| Do | .. | 2 |
| Native tan liquor, strong from covered pit | .. | 8 |
| Fresh tan liquor | .. | 8 |
| Artesian-well water as delivered at tannery | .. | 15 |
| Suspender liquor (my experiment) mixed with 10 per cent. native tan liquor | .. | 3 |
| Do | .. | 6 |
| Liquor from layer No 1 (my experiment †) | 3 | .. |
| Do | 13 | |
| Liquor from layer No. 1 (my experiment), from covered pit | .. | 15 |
| Fresh tan liquor made with artesian water | 10 | .. |

† In this case the workmen were allowed to contaminate the liquor by wading in it with bare feet still wet with liquors from polluted vats, according to the usual practice. Contrast the three days required to liquefy the serum with the following experiment where thirteen days were required. The only difference is that in the second case I insisted that the workmen first wash their feet in clean water before entering the vats.

Infusions of fresh camanchile tan bark in pure water are generally practically devoid of liquefying bacteria, as liquefaction of inoculated serum and gelatin media occurs only after from forty-two to seventy-five days of incubation. However the infusion of this tan bark is quite neutral in its action toward liquefying bacteria. It does not kill them. On the other hand, bacteria do not grow in it except when there is enough proper nourishment present in the form of other suitable substances. In the latter case the multiplication and activity are great in a warm climate.

The tannins, like common salt, do not destroy bacteria, but check the putrefaction of hide substance. Common salt prevents the putrefaction by extracting water from the hide, while the tannins convert the hide into imputrescible leather. The work

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of the salt is transient, while that of the tannins is permanent.

An experiment was performed to determine the resistance to, and growth of, liquefying bacteria in camanchile bark infusion at a temperature between 27° and 32° C. Tan infusions were inoculated with tannery liquors, and subsequently a loopful of each was transferred to serum and gelatin media tubes. The periods of time required for liquefaction are given in Table XIV.

TABLE XIV.—EFFECT OF TAN INFUSIONS ON LIQUEFYING BACTERIA.

| Liquor tested | Days to liquefy | | | |
|---|---|---|---|---|
| | Serum | | Gelatin | |
| | Incipient liquefaction | Complete | Incipient liquefaction | Complete |
| Fresh control infusion | ..... | 42 | ..... | ..... |
| Control infusion 1 day old | ..... | ..... | 23 | 26 |
| Control infusion 3 days old | ..... | ..... | (‡) | (‡) |
| Infusion 1 day after inoculation with river water | 5 | 15 | ..... | ..... |
| Do | ..... | ..... | 1 | 8 |
| Infusion 3 days after inoculation with river water | 4 | 10 | ..... | ..... |
| Do | ..... | ..... | 10 | 14 |
| Infusion 6 days after inoculation with river water | 5 | 11 | ..... | ..... |
| Do | ..... | 10 | ..... | ..... |
| Infusion 1 day after inoculation with native tan liquor | 4 | 6 | ..... | ..... |
| Do | 5 | 6 | ..... | ..... |
| Infusion 8 days after inoculation with native tan liquor | 3 | 4 | ..... | ..... |
| Do | ..... | ..... | 10 | 12 |
| Infusion 3 days after inoculation with native tan liquor | 4 | 10 | ..... | ..... |
| Infusion 6 days after inoculation with native tan liquor | ..... | ..... | 4 | 10 |
| Layer liquor No. 1 (my experiment) | ..... | ..... | ..... | 3 |
| Do | 4 | 9 | ..... | ..... |

‡ No liquefaction in 75 days.

In this experiment the gelatin tubes were more resistant to the action of the liquefying bacteria than the serum tubes, thus illustrating the fact which must always be borne in mind by a tanner that blood remaining in the hides and skins is one of the causes of speedy putrefaction. Even with fresh and strong tan infusion liquefying and other bacteria will thrive and are sure to do mischief provided there is enough proper food for them.

The waste of tanning material is due almost solely to the

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Filipino practice of chopping rather than grinding the bark. As the price of camanchile bark is steadily rising and constitutes an item of very large expense to the tanner, any methods for more effective utilization of the material would be very practical. Tan bark is never ground, but chopped with a heavy, curved knife into pieces about 3 by 4 centimeters in size, which are much too large to permit complete extraction of the tannin. This practice results in a large waste of material, as may be seen from determinations included in Table XV.

TABLE XV.—ANALYSES OF FRESH AND "SPENT" CAMANCHILE BARK.

| Condition of bark | Moisture | Only dry basis | | |
|---|---|---|---|---|
| | | Total extract | Non-tannins | Tannins |
| | Per cent. | Per cent. | Per cent. | Per cent. |
| Fresh | 10.34 | 34.77 | 9.41 | 25.36 |
| Used | 12.64 | 23.63 | 8.31 | 15.32 |

In this case only 39.6 per cent. of the total tannings contained in the bark was used by the tanners, while the remaining 60.4 per cent. was thrown away in the "spent" bark.

Undertannage of leather is one of the chief causes of an unsatisfactory product. This is produced in part by insufficient plumping of the hides, in part by the use of coarse bark in making infusions, but principally because of false economy in the use of the bark. In examining the tan liquors in any Filipino tannery, it will be noted that they are uniformly much too weak, except at the very beginning of the process. In fact, the first tan liquors, corresponding to suspender liquors, are the strongest which are used in the process. This, of course, produces rapid tanning of the surface and, to a great extent, prevents thorough tanning of the interior of the hide.

In determining the percentage of tannin in the tan liquors, specific gravity tests were found to be very unreliable, especially in the case of the older liquors. Large quantities of mineral matter are introduced from the brackish river water and from the hides themselves which are insufficiently delimed. Deliming is rarely effective, as is clearly indicated by the red coloration produced when a drop of a phenolphthalein solution is placed on the surface of the hide.

A piece of delimed hide just ready for the tan pits, after being placed in river water with sufficient formaldehyde to

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preserve it, was found to be still well impregnated with lime after forty-eight hours. The specific gravity of the river water itself is 1.029. Table XVI shows the specific gravities of tan liquors at various stages of the process.

TABLE XVI.—SPECIFIC GRAVITIES OF FILIPINO TAN LIQUORS.

| Sample No. | Age | Contact with pelts | Specific gravity |
|---|---|---|---|
| | *Days* | *Days* | |
| 1 | 5 | 1 | 1.022 |
| 2 | 4 | — | 1.022 |
| 3 | 6 | — | 1.022 |
| 4 | 8 | 5 | 1.021 |
| 5 | 3 | — | 1.011 |
| 6 | 6 | — | 1.016 |
| 7 | 8 | 5 | 1.019 |

Analyses of tan liquors are given in Table XVII.

TABLE XVII.—ANALYSES OF FILIPINO TAN LIQUORS.

| Sample No. | Stage of process | Specific gravity | Acidity as grams acetic acid per 100 cc. | Grams per 100 cc. of the liquor | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Ash | Organic matter | Suspended matter | Non-tans | Tannin |
| 1 | First day | 1.010 | 0.15 | 0.79 | 1.59 | 0.38 | 1.39 | 0.61 |
| 2 | Fourteenth day | 1.018 | 0.09 | 2.22 | 1.64 | 0.47 | 3.30 | (1) |
| 3 | Sixth week | 1.018 | 0.17 | 1.64 | 2.41 | 1.41 | 2.59 | (1) |
| 4 | Third day, 20 per cent. extra strength | 1.022 | 0.06 | 2.03 | 1.86 | (2) | 3.22 | 0.67 |
| 5 | Half completed | 1.019 | — | — | — | — | 3.20 | 0.34 |

[1] Trace. [2] Undetermined.

The tannin in these liquors is strikingly low, and the non-tans, especially the mineral matter, are very high, as is to be expected when brackish water is used. Analyses of the ash of Filipino tan liquors are given in Table XVIII.

In addition to the mineral matter the organic non-tans are in considerable part nitrogenous materials. The quantity of nitrogenous materials in representative tan liquors is shown in Table XIX.

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TABLE XVIII.—ANALYSES OF THE ASH OF FILIPINO TAN LIQUORS.

[Grams per 100 cc. of liquors.]

| Sample No.[1] | Silica ($SiO_2$) | Oxides of iron and aluminium ($Fe_2O_3$ $Al_2O_3$) | Oxide of iron ($Fe_2O_3$) | Calcium oxide (CaO) | Magnesium oxide (MgO) | Sulphuric anhydride ($SO_3$) | Chloride and carbonate of sodium plus phosphoric anhydride |
|---|---|---|---|---|---|---|---|
| 1 | 0.006 | 0.026 | —— | 0.061 | 0.034 | 0.039 | 0.62 |
| 2 | 0.009 | —— | 0.131 | 0.093 | 0.145 | 0.064 | 1.77 |
| 3 | 0.030 | 0.089 | —— | 0.133 | 0.102 | 0.074 | 1.21 |
| 4 | 0.008 | 0.039 | —— | 0.135 | 0.167 | 0.078 | 1.60 |

[1] The samples correspond to the tan liquors in the previous table.

TABLE XIX.—NITROGEN CONTENT OF FILIPINO TAN LIQUORS.

[Grams per 100 cc. of the liquors.]

| Sample No. | Nitrogen as saline ammonia | Equivalent hide substance | Total Nitrogen | Equivalent hide substance |
|---|---|---|---|---|
| 1 | 0.0430 | 0.234 | 0.062 | 0.343 |
| 3 | 0.0405 | 0.223 | 0.077 | 0.422 |
| 5 | 0.0980 | 0.540 | 0.137 | 0.754 |

Tests show that extract of camanchile bark contains considerable quantities of nitrogenous material, and a correction must, therefore, be made. Table XX gives the nitrogen contents of the samples in the preceding table and of a fresh camanchile bark infusion calculated as hide substance in per cent. of total solids.

TABLE XX.—NITROGEN CONTENTS OF FILIPINO TAN LIQUORS CALCULATED AS PERCENTAGE OF TOTAL SOLIDS.

| Sample No. | Saline ammonia as hide substance | Total nitrogen as hide substance | Organic nitrogen as hide substance |
|---|---|---|---|
| 1 | 11.70 | 17.17 | 5.47 |
| 3 | 8.45 | 15.99 | 7.54 |
| 5 | 15.20 | 21.38 | 6.18 |
| Fresh | 1.74 | 6.60 | 4.86 |

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## Demonstration of Simple, Efficient Improvements in the Filipino Tanning Process.

Bearing in mind the facts that Filipino tanners do not possess sufficient capital to purchase expensive equipment and that they are indisposed to abandon completely the methods they have used for generations and the cheap labor which they can obtain, an endeavor was made to find simple, inexpensive methods of improvement. In the main this was accomplished without serious difficulty. The improvements in the process are very striking, although no doubt they could be still further increased, especially by additional modification of equipment. The following method was put into effect in a Filipino tannery which was then operating under the old methods. This was done as an object lesson, in spite of the unfavorable circumstances which it was anticipated would be encountered. A leather resulted which was odorless, firm, and entirely satisfactory as a sole leather. For this purpose nine hides were chosen as indicated in Table XXI.

TABLE XXI.—Hides Used in Tanning Experiments.

| | Kilos |
|---|---|
| **Australian cattle hide:** | |
| No. 1 | 16.5 |
| No. 2 | 23.5 |
| No. 3 | 24.0 |
| **Chinese cattle hide:** | |
| No. 1 | 19.0 |
| No. 2 | 16.0 |
| No. 3 | 19.0 |
| No. 4 | 21.5 |
| No. 5 | 18.5 |
| No. 6 ‡ | 25.5 |

‡ Carabao.

The hides were washed in fresh, clean water supplied from a near-by artesian well. The washing was repeated five times and, together with soaking, required seven hours.

This water is almost sterile as it comes from the well and was very little contaminated in carrying to the tannery. The hides were next placed in a pit with 40 liters of lime and 400 liters of artesian water, and were left for eight days, during which

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time they were handled five times.[7] They were then fleshed and dehaired and placed in a 1 per cent. phenol solution for twenty-four hours. A bath in a 0.2 per cent. solution of sulphuric acid for fifteen minutes followed, for the purpose of neutralizing the surface lime of the pelts. They were placed in a suspender containing very weak, fresh tan liquor, with a specific gravity of about 1.000 at ordinary temperature, and whose strength and acidity were increased every day during ten days up to 1.004 specific gravity and 0.2 per cent. acetic acid.

TABLE XXII.—ANALYSIS OF THE ARTESIAN-WELL WATER.

[Numbers represent parts per million.]

| | |
|---|---|
| Physical characters | normal |
| Reaction | alkaline |
| Total solids | 274.0 |
| Appearance on ignition | little blackening |
| Free or saline ammonia | 0.074 |
| Organic or albuminoid ammonia | 0.026 |
| Chlorine | 4.8 |
| Nitrogen as nitrates | nil |
| Nitrogen as nitrites | nil |
| Silica ($SiO_2$) | 45.0 |
| Oxides of iron and aluminium | trace |
| Oxide of calcium (CaO) | 6.0 |
| Oxide of magnesium (MgO) | little |
| Sulphuric anhydride ($SO_3$) | trace |
| Total hardness | 10.7 |
| Permanent | 10.7 |
| Bicarbonic acid radical ($HCO_3$) | 183.0 |
| Carbonic acid radical ($CO_3$) | 15.0 |

After ten days in the suspender liquor the hides were removed and laid in another clean pit with 50 kilograms of half-used tan bark and sufficient tan liquor of specific gravity 1.006 to cover the hides. On the fourth day they were handled, and 50 kilograms of fresh bark were added. On the ninth day they were again handled, with an addition of 100 kilograms of fresh tan bark. On the twenty-fifth day they were again handled, with an addition of 130 kilograms of fresh bark; on the forty-fifth day with 210 kilograms, and on the sixty-fourth day with

[7] The only advisable changes in the Filipino method of liming would be to use from one to three changes of lime liquor and to keep the lime pit clean.

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162 kilograms. The specific gravity of the liquors was taken after each handling.

TABLE XXIII.—SPECIFIC GRAVITY OF HANDLED LIQUORS.

| Handling No. | Specific gravity of tan liquor |
|---|---|
| 1 | 1.006 |
| 2 | 1.006 |
| 3 | 1.007 |
| 4 | 1.012 |
| 5 | 1.017 |
| 6 | 1.020 |
| 7 | 1.022 |

While in the suspenders and during the first forty-five days in the laying pit the rate of tannage was rapid. Thereafter it decreased markedly, as is shown in Table XXIV.

TABLE XXIV.—ANALYSIS OF LEATHER SAMPLES TAKEN AT DIFFERENT TIMES DURING TANNAGE, AFTER THE TWENTY-FIFTH DAY IN THE LAYING PIT.

| Day | Kind of hide | Moisture | Parts per 100 of $H_2O$ free material | |
|---|---|---|---|---|
| | | | Hide substance | Tanning matters and ash |
| | | Per cent. | | |
| Twenty-fifth | Cattle | 17.3 | 58.7 | 41.3 |
| Forty-fifth | do | 16.9 | 51.0 | 49.0 |
| Sixty-fourth | do | 14.5 | 50.8 | ‡49.2 |
| Seventy-second | do | 14.1 | 50.1 | 49.9 |
| Do | Carabao | 14.2 | 53.1 | 46.9 |

‡ The owner of the tannery at this point unfortunately added 5 fresh pelts to the pit, thereby reducing the strength of the tan liquor and the degree of tannage.

The rate of tannage of the carabao hide is noticeably slower than that of the cattle hides on account of its thickness. Such thick hides should consequently always be tanned separately. The increase in strength of the tan liquors, as indicated in Table XXIV, was by no means as rapid as was to be desired. However, as no means were available for grinding the bark, it was not feasible to avoid this objectionable feature. In addition, the process was considerably disturbed by the real or fancied necessities of the owner, who used tan liquor from the layer pit for other hides.

On the seventy-second day the goods were taken from the pit, piled upon a beam to drain, brushed, wiped, and lightly oiled on the grain. When half-dried under the shed, where they hang

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from one to five days according to weather conditions, they were laid in a pile to temper. This allows the moisture to distribute itself equally throughout the hides. They were then struck out with a striking pin to smooth and flatten the grain and were hung under the shed further to dry. A second striking followed. They were then rolled with a smooth, hardwood roller provided with a suitable carriage and properly weighted, first with a light weight and a slightly moist grain, and then with a heavy weight and a nearly dry grain. After being rolled, the goods were dried rapidly with free circulation of air and finally polished with a brush by hand.

The hides so obtained were free from all of the principal defects of the native leather. They displayed no odor nor evidence of putrefaction at any point. The loss of hide substance was much smaller and the degree of tannage much higher, as indicated by Table XXV, which shows the weight of the native leather and that produced by the improved process.

TABLE XXV.—WEIGHTS OF TANNED HIDES.

| Weights of Filipino tanned hides | | Weights of leather from hides tanned in this experiment ‡ | |
|---|---|---|---|
| Australian cattle leather | Chinese cattle leather | Australian cattle leather | Chinese cattle leather |
| Kilo. | Kilo. | Kilo. | Kilo. |
| 11.5 | 9.0 | 11.5 | 13.0 |
| 10.0 | 10.0 | 17.0 | 11.0 |
| 12.5 | 9.0 | 16.5 | 13.0 |
| 11.0 | 10.5 | .... | 14.0 |
| 10.5 | 9.0 | .... | 12.0 |
| 12.0 | 10.0 | .... | 20.0 |
| 10.5 | 9.0 | .... | .... |
| 13.0 | 10 0 | .... | .... |

‡ These hides are arranged in the same order as in the list of raw hides in table XXI.

The average weight of hides tanned by the improved process is approximately 32 per cent. greater than that of those ordinarily produced. In other words, the Filipino tanner obtains about 3 kilograms of leather from 6 kilograms of green pelt, while by the improved process this yield of leather is increased to about 4 kilograms of higher grade product. Table XXVI shows the degree of tannage in native leathers as compared with those produced by the improved process.

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TABLE XXVI.—CHEMICAL ANALYSIS OF LEATHER.

| | Moisture Per cent. | Parts per 100 of water-free material: Hide substance | Tanning matters and ash |
|---|---|---|---|
| Improved product ... | 14.1 | 50.1 | 49.9 |
| Filipino product..... | 16.5 | 61.4 | 38.6 |
| Do..... | 16.3 | 62.9 | 37.1 |

The color and grain of the hides produced by the improved process, while not perfect, were entirely satisfactory for local market conditions, and the actual increase in the value of the goods by these improvements far exceeded the small increased cost of putting them into effect. Local tanners were alarmed by the large quantities of tan bark which were added to the laying pit. It was difficult for them to realize that no tannin is wasted, but that the use of old tan liquor, suitably diluted, is to be preferred for fresh hides, so that the entire excess of tannin is eventually utilized. The only actual increase in cost lies in the added labor in finishing the leather. For this expenditure the tanner will be amply repaid. Finally, the practice of chopping bark by hand cannot be too severely condemned as wasteful of tanning material and labor alike. A mill for grinding the bark would repay its entire cost in a few weeks of operation.

An experiment with ten hides was carried out substantially as above outlined, except that mangrove bark was used exclusively in the layer pits after lying in suspender liquor of camanchile. The resulting leather was orange brown, which is not objectionable. The texture was firmer than that of camanchile leather. The partial substitution of mangrove for camanchile is to be recommended as rapidly as the local leather buyers can be induced to accept slightly darker colored goods.

## SUMMARY.

1. The tanning industry in the Philippine Islands amounts to about 1,800,000 pesos per annum and can be greatly extended.

2. It has been shown that improvements can be put into effect in a Filipino tannery without modification of the equipment and with little increase in expense, which will yield about 32 per cent. more leather of a higher grade than that now produced. Leather produced by the improved process is firm, of a satisfactory color and grain, and free from the disagreeable odor or evidence of putrefaction, and other principal defects of native leather.

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3. A great economy in both labor and material can be effected in the Filipino process by grinding the tan bark in a mill instead of chopping it by hand. The tanning materials never become satisfactorily extracted from chopped bark, and the resulting waste is very great.

4. Good, moderately colored leathers can be produced by combining camanchile and mangrove at a considerably decreased cost.

## ABSTRACTS

**Reminiscences of Dutch West Borneo.**—A. T. HOUGH, *L. T. R.*, 1915, pp. 458-60. Tan barks in the tropics are with few exceptions poorer in quality in the rainy season. Green bark is easier to extract than dry. The water of condensation from the evaporating plant is an important factor in the practical economy of the extract plant. It contains 1 or 2 parts iron per 100,000 and is distinctly acid, due to organic acids from the tan liquors. This water yields a better colored product with mangrove bark than pure water, probably due to the bleaching effect of the acids and the neutralization of alkaline salts. The iron is retained in the tail leach by the mangrove bark which is spongy. The fuel used is mangrove wood, together with spent bark. Exports of mangrove extract from Pontianak were as follows: 1912, $34,000; 1913, $69,600; 1914, $78,600.

**Cattle Industry in Rio Grande do Sul.**—Vice-Consul R. L. KEISER, in *Commerce Reports*, Supplement 40a, April 6, 1916. (Rio Grande do Sul is the southernmost State of Brazil.) The State has good grazing grounds, and more than one-third of the cattle of Brazil are raised here. Up to August, 1914, Rio Grande do Sul had direct steamer communication with Europe, by the Hamburg-American Line. Since that time, no direct communication with Europe or North America has been available except by sailing vessels. In spite of this, the exports to the United States have rapidly increased since the closing of Hamburg. The great bulk of the hides, skins and glue stock exported from this State has for many years gone to Germany. The total exports to the United States for the first six months of 1915 were four times as great as for the entire year of 1914. Exports of hides have decreased during the last five years, due to a rapid decrease in the number of cattle slaughtered, and the growth of a domestic tanning industry. The types of cattle raised in the State are mostly descended from those imported by the early Portuguese settlers. Lack of transportation facilities and consequent low selling prices gave no stimulus to efforts to improve the stock. Recent increase in values of cattle all over the world has given an impetus to the industry, and the conditions of production have been much improved. In the past, heavy losses were incurred from floods in the low lands, from epidemics due to enfeebled condition due to lack of salt, and from insufficient protection

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in winter. Experiments in the introduction of blooded stock have not always been successful, the imported animals being difficult to acclimate. The percentage of Durham and Hereford stock in some districts is now considerable. In the eight counties bordering on Uruguay, the average number of cattle is 117 per square mile. From 500,000 to 800,000 cattle annually are slaughtered in Rio Grande do Sul in the production of jerked beef. A project is on foot to establish a packing house at Rosario. In May, 1914, the export duty on live cattle was suspended. This amounted to $2.50 per head on cattle shipped out of Brazil, and 75 cents a head for cattle shipped to other States of Brazil. The number of sheep in Rio Grande do Sul has nearly doubled in seven years. Their value more than doubled, being estimated at $9,684,000 in 1915. The sheep are mostly of good breeds. Wool is exported through Uruguay. Hogs are raised in that part of the State near Porto Allegre. This industry has resulted from the lack of cheap transportation for grain, which is now being fed to hogs. The lard industry has thus become very important, amounting in 1915 to more than $8,500,000.

**Sabadilla in the War.** Consul HOMER BRETT, La Guaira, Venezuela, Mar. 21, in *Commerce Reports*. A press telegram from England recently published in Caracas stating that the asphyxiating and tear-producing gases used in the present war are made from "Sabadilla," a product exported only from Venezuela, has caused considerable discussion in which the following facts have been brought out:

Sabadilla, known locally as "Cevadilla," a diminutive of the Spanish word Cebada, meaning barley, is the name of a plant of the lily family, botanically called "Veratrum sabadilla Retztus," occurring only in Venezuela and Mexico. The highly poisonous seeds have long been used in medicine The substances produced from sabadilla seed are cavadine, or crystallized veratric, an alkaloid with the formula $C_{32}H_{49}O_9N$; veratric acid ($C_8H_{10}O_4$), and Sabadalline ($C_{34}H_{53}O_8N$). This last is an amorphous, pleasant smelling alkaloid, that accelerates the beating of the heart. While nothing is known here as to its use in the production of war gases, it is a fact that sabadilla dust irritates the eyes, the throat, and especially the nose so much that laborers working with it are obliged to wear protecting masks. Sabadilla powder is used by cattle raisers in this country as an insecticide with excellent results. It is stated that in Europe it is used in the manufacture of disinfectants, and that in the Balkan States and Russia it is employed in tanning fine leathers and as a mordant for dyes. The first exportation from Venezuela was made to Hamburg 25 or 30 years ago The foreign demand has never amounted to more than 5,000 sacks annually. Whenever production passes beyond this point the price has fallen below the cost of gathering. It is not a cultivated crop, but might become such if new uses were discovered which would cause an increased and regular demand. It grows in the vicinity of Caracas and is exported from La Guaira.

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## THIRTEENTH ANNUAL MEETING.

The thirteenth Annual Meeting of the American Leather Chemists Association will be held at the Marlborough-Blenheim,

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Atlantic City, N. J., on Thursday, Friday and Saturday, June 1, 2 and 3, 1916, beginning at 10 o'clock on Thursday morning.

## PROGRAM.

### Thursday Morning, June 1, 1916.

Opening Remarks by the President.....Dr. Louis E. Levi.

Report of the Secretary-Treasurer.....H. C. Reed.

Committee Reports.

### Thursday Afternoon, June 1, 1916.

"Cure and Disinfection of Hides."

### Friday Morning, June 2, 1916.

Committee Reports.

Address .....H. C. Reed.
"Accuracy of the Aniline-Hydrochloric Acid Method for the Detection of Sulphite-Cellulose in a Mixture with Other Tanning Materials."

Address .....Dr. Lloyd Balderston.
"Wear Resistance of Sole Leathers."

### Friday Afternoon, June 2, 1916.

Papers on the "Cure and Disinfection of Hides" with discussion.

Address .....Byron E. Parks.
"Fuel Value of Spent Tan Bark."

### Saturday Morning, June 3, 1916.

Committee Reports.

Executive Session of the American Leather Chemists Association.

Election of Officers.

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## THE ACID–GELATINE EQUILIBRIUM.*

*By H. R. Procter and J. A. Wilson.*

In an earlier paper by one of us (*Transactions*, 1914, 105, 313, this J., 1914, pp. 207-25) it was shown that gelatine forms hydrolizable salts with acids, that swelling is due to the ionization of these and the osmotic pressure so produced, and that an equilibrium results, in which the concentrations of anion, hydrion, and ionized gelatine-salt can all be expressed as functions of the concentration of acid in the external solution, within the limits of experimental error. In this earlier paper the concentration of the ionized gelatine chloride in the equilibrium gelatine-hydrochloric acid was shown to be approximately $Clg = \sqrt{0.02x + 0.0002}$, where $Clg$ was the chlorine ionized from the gelatine-salt, and $x$ the concentration, in terms of normality, of the external hydrochloric acid. (Through an error $Clg$ was given as $\sqrt{2x + 0.02}$, but all actual calculations were made from the above formula.) It was also assumed that the numerical values in the expression were constants, as those adopted sufficiently closely represented the experimental results then quoted, but closer theoretical investigation has shown that this is not strictly the case, but that both $Clg$ and $x$ are functions of a quantity $e$, which is the difference in osmotic pressure between two phases of which the ionic products are equal, but in one of which the factors are unequal; and that it is this difference which causes the swelling of the jelly.

In the paper cited the hydrochloric acid and gelatine salt were for the sake of simplicity supposed to be wholly ionized, and as the ionization in both cases is very high and the solutions were dilute, such an assumption was quite justifiable as regards experimental results. In the closer theoretical examination which we now propose, however, we must define the concentrations as referring only to the actual ions; and we shall again first consider the comparatively simple case of hydrochloric acid and gelatine, where the ionization is in reality almost complete.

The following system of notation will be employed:

At equilibrium:

In the external solution:

$$x = [H^+] = [Cl']$$

* Transactions of the Chemical Society, (England).

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in the jelly phase:

$y = [H^+]$.

$z$ = concentration of gelatine ions.

$y + z = [Cl']$.

$a$ = concentration of non-ionized gelatine chloride.

$g$ = sum of concentrations of gelatine, gelatine chloride, and gelatine ions.

$e$ = excess of concentration of diffusible ions of the jelly over that of the external solution.

$V$ = volume of the jelly in cc.

All concentrations are expressed in gram-equivalents per liter. In all experiments 1 gram of dry gelatine was immersed in 100 cc. of the acid solution and allowed to remain for forty-eight hours to reach equilibrium, the temperature being about 20° in each case. The concentration of acid in the external solution was determined by titration, and that in the jelly by titrating the solution expelled from the jelly by the addition of salt, and with these, knowing the initial concentration of the acid and the percentage of ionization of acid in the external solution, the actual ionic concentrations can be calculated.

In a two-phased equilibrium, such as the present, two different equations must be fulfilled. It is necessary that the products of hydrion and chloridion should be equal in the two phases; that is:

$$x^2 = y(y + z) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This is not only proved by the thermodynamical equation of Donnan, quoted in the earlier paper (*loc. cit.*), but also follows from the ordinary laws of ionization, since the non-ionized portion of hydrochloric acid which, although small, must exist, takes no direct part in the equilibrium, and must be equal in both phases since the jelly is permeable to it, and

$$x^2 = [H_1^+] \times [Cl'_1] = K[HCl] = [H_2^+] \times [Cl'_2] = y(y + z).$$

It was, however, previously pointed out that the equations

$$\begin{cases} x^2 = y\,(y + z) \\ 2x = 2y + z \end{cases}$$

cannot simultaneously be fulfilled, since in the jelly $[H^+]$ and $[Cl']$ are necessarily unequal, the chloridion being greater than the hydrion by the amount $z$, and the sum of the sides of an un-

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equal rectangle is necessarily greater than that of the sides of a square of equal area (see Fig. 1). In other words, $2y + z$ is greater than $2x$ by an amount we shall call $e$, and the corrected equation becomes:

$$2x + e = 2y + z \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The concentration of diffusible ions of the jelly is therefore greater by $e$ than that of the outer solution. It is obvious, since water and hydrogen chloride can pass freely into the jelly, that there must be some force equal to and opposing the osmotic pressure produced by this excess $e$ of concentration at equilibrium, for otherwise the jelly would tend to swell to infinity.

Before attempting to speculate about the nature of this opposing force, we must consider its mathematical relations to the other concentrations of the equilibrium as defined by equations (1) and (2). The general theory of the equilibrium as developed in earlier papers (*Koll.-chem. Beihefte*, 1911, 2, 243, this J., 1911, pp. 270-308 and 1914, pp. 207-25) is that when gelatine is placed in dilute acid it absorbs it freely and forms a hydrolizing salt, the proportion of which to the whole gelatine-base present is determined by the hydrolysis equation. The gelatine-salt, like other salts, is highly ionized into the anion and a colloid cation, which either from polymerization or other causes peculiar to the colloid state cannot diffuse and exerts no measurable osmotic pressure, whilst its anion is retained in the jelly by the electro-chemical attraction of the colloid ion, but exerts osmotic pressure which, on the one hand, causes the mass to swell with absorption of the external solution, and, on the other, expels a portion of the acid, both anion and hydrion, from this solution absorbed, the result in equilibrium being that the jelly is poorer in hydrion and more concentrated in anion than the external acid solution, the difference of concentration between anion and hydrion in the jelly being, of course, equal to the ionized anion of the gelatine-salt, and electrically balanced by the positive gelatine ions; whilst the hydrion concentration in the jelly is less concentrated than that of the outer solution by the amount of acid expelled, which may be called $v$ (the isotonic volume of hydrion or chloridion expelled at a concentration of $x$); $v$ bears the simple

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relation to $y$ that $y + v = x$ and the concentration of ionized gelatine chloride, $z = 2v + e$.

By solving simultaneously equations (1) and (2) the following interesting relations are derived:

$$x = y + \sqrt{ey} = \sqrt{y^2 + yz} = \frac{z^2 - e^2}{4e}$$

$$y = \frac{-z + \sqrt{z^2 + 4x^2}}{2} = \frac{2x + e - \sqrt{4ex + e^2}}{2} = \frac{(z-e)^2}{4e}$$

$$z = \frac{x^2 - y^2}{y} = \sqrt{4ex + e^2} = e + 2\sqrt{ey}$$

$$e = \frac{(x-y)^2}{y} = z + 2y - 2\sqrt{y^2 + yz} = -2x + \sqrt{4x^2 + z^2}$$

These relations can be represented graphically for any value of $x$, as is shown in Fig. 1.

Any one variable can be derived in terms of any other two, but in no case, from only the two equations given, can an equation be derived containing only two variables. As was pointed out previously, however, $z$ was found from experiment to be equal approximately to $\sqrt{0.02x + 0.0002}$, which bears a resemblance to one of the derived equations, namely, $z = \sqrt{4ex + e^2}$. Putting $e = 0.005$, we get $z = \sqrt{0.02x + 0.000025}$, which is strikingly like the one obtained empirically, but gives low values for concentrations less than $x = 0.03$. Theoretical considerations rendered it improbable that $e$, considered in the general way in which we have done, could be a real constant, but it is difficult to obtain a smooth experimental curve from the formula $e = \frac{(b-y)^2}{y}$, because small errors in $y$ correspond with large errors in $e$, and it is not possible to determine $y$ in the most dilute solutions with very great accuracy by volumetric methods.

It occurred to us, however, that if we could incorporate the volume of the jelly, which can be determined with great accuracy, into an equation containing only two other variables, it would at once be possible to calculate any variable from $V$ and $x$ only. It was found that the theory could be summed up in the form of such an equation, which could readily be subjected to the rigid test of experiment. The notation used is that mentioned earlier in the

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paper. The degree of ionization of any given electrolyte, MN, is often expressed by the formula $[M^+] \times [N'] = K[MN]$, where $K$ may be nearly constant, as in the case of acetic acid, or a variable, as in the case of highly ionizable electrolytes. In the fol-

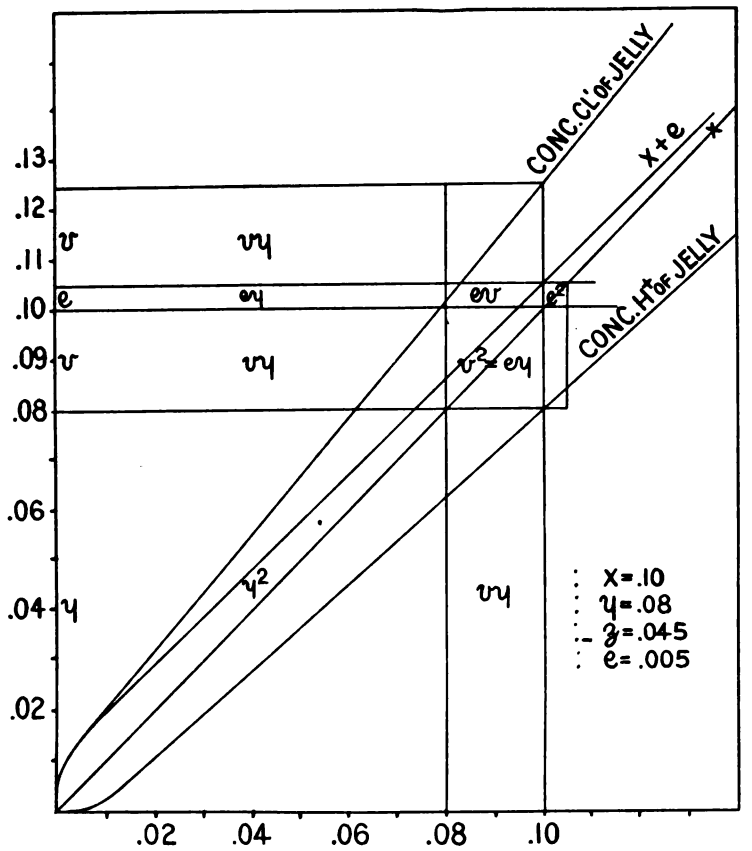


FIG. 1.
Curves of Concentration.

lowing, gelatine chloride is considered to be ionized into gelatine ion and chloridion, and the gelatine ion to be ionized still further into gelatine molecule and hydrion. A similar case would be the ionization of ammonium chloride into ammonion, and chloridion

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and the further ionization of the ammonion into ammonia and hydrion. We may therefore write:

$$(a)\ [\text{gelatine ion}] \times [Cl'] = K[\text{gelatine chloride}] \text{ or } z(y+z) = Ka.$$

$$(b)\ [\text{gelatine molecule}] \times [H^+] = K'[\text{gelatine ion}] \text{ or } y(g-a-z) = K'z.$$

By solving $(a)$ and $(b)$ simultaneously to remove the term in $a$:

$$(c)\ Kgy = y^2z + Kyz + yz^2 + KK'z.$$

Taking Procter's figure of 839 for the molecular weight of a unit of gelatine, 1 gram of gelatine represents 0.00119 gram-equivalent. Therefore at any volume:

$$(d)\ g = \frac{1.19}{V}$$

Substituting $(d)$ in $(c)$ and simplifying:

$$(e)\ V = \frac{1.19\,Ky}{z(y^2 + Ky + yz + KK')}$$

Or in terms of $x$ and $y$:

$$(f)\ V = \frac{1.19\,Ky^2}{(x^2-y^2)(x^2+Ky+KK')}.$$

The value for $K'$ has been considered to be so small that neglecting it should produce no appreciable errors in concentrations greater than $x = 0.005$, so that for these more concentrated solutions the equation reduces to:

$$(g)\ V = \frac{1.19\,Ky^2}{(x^2-y^2)(x^2+Ky)}.$$

Now $K$ has been assumed, with good reason, to be nearly equal to the ionization-constant of hydrochloric acid for corresponding concentrations. It will be noted from the above equation that small errors in the value of $K$ will produce negligible errors in the calculations so long as the value of $Ky$ is considerably greater than that of $x^2$, and such a condition does obtain in these more concentrated solutions so long as $K$ is the ionization-constant of a strong electrolyte. For the present set of calculations, then, it will be permissible to take $K$ as the ionization-constant of hydrochloric acid, which is known approximately for any given concentration. Moreover, since it has been shown that, in these more concentrated solutions, almost all the gelatine has been con-

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verted into the monochloride, we are justified in taking $K$ as the ionization-constant of hydrochloric acid at concentration $g$, where $g$ is simply $\frac{1.19}{V}$. Now from experimental values for $V$ and $x$ it is possible to calculate values for $y$, which should not differ from the value obtained from experiment by more than would be attributed to experimental error. The results are given in Table I.

TABLE I.

| Determined as noted above * | By experiment | | | Calculated |
|---|---|---|---|---|
| $K$ | $V$ | $x$ | $y$ | $y$ |
| 0.95 | 16.9 | 0.262 | 0.228 | 0.237 |
| 0.94 | 17.5 | 0.220 | 0.186 | 0.195 |
| 0.88 | 20.2 | 0.174 | 0.145 | 0.152 |
| 0.85 | 21.6 | 0.153 | 0.123 | 0.132 |
| 0.85 | 21.6 | 0.130 | 0.105 | 0.108 |
| 0.83 | 22.4 | 0.108 | 0.080 | 0.087 |
| 0.80 | 24.1 | 0.087 | 0.066 | 0.068 |
| 0.75 | 25.9 | 0.064 | 0.049 | 0.047 |
| 0.65 | 34.3 | 0.0386 | 0.028 | 0.026 |
| 0.56 | 45.6 | 0.0165 | 0.0084 | 0.0084 |
| 0.55 | 49.4 | 0.0118 | 0.0057 | 0.0050 |
| 0.50 | 56.4 | 0.0071 | 0.0020 | 0.0022 |

* These calculations are based on the figures of Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, 33, 781) and those of Noyes and Falk (*ibid.*, 1912, 34, 454).

The agreement between experimental and calculated values bears out the theory remarkably well, the differences being not greater than was to be expected, considering the difficulties in titrating small quantities of solutions containing traces of organic matter. We feel that values for $e$ calculated from $V$ and $x$ by this formula will be approximately correct. Of course, it is evident that in the very dilute solutions $K'$ ceases to be a negligible quantity. Preliminary experiments with the hydrogen electrode show that $K'$ is of the order of 0.00015, which fully justifies our assumptions in neglecting it for the higher concentrations.

In Figs. 2 and 3 curves are given for the various variables as functions of $x$. The values for $V$, $x$ and $y$ were obtained directly from experiment, whilst those of $z$ and $e$ were calculated by means of the above formula. It will be noted by reference to

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Figs. 2 and 3 that *e* apparently varies directly as the volume. Such a relation, if it could be proved, would simplify all other

FIG. 2.

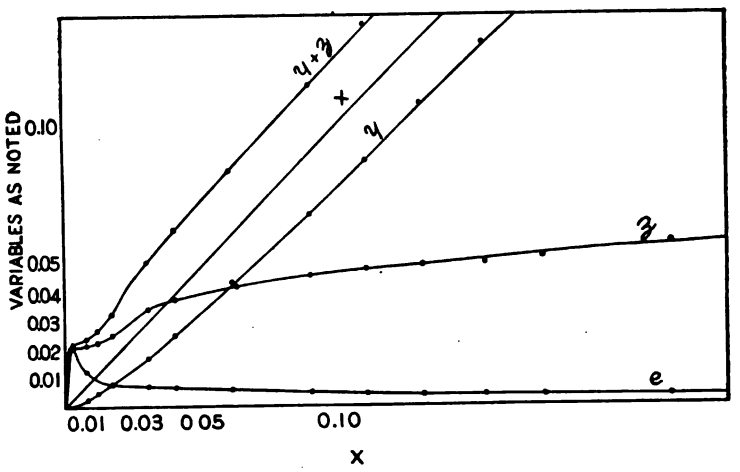
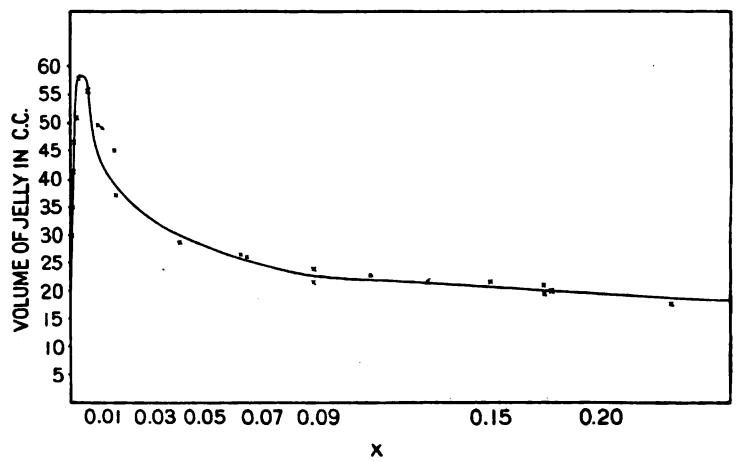



FIG 3




relations to the extent that any variable could be expressed, with suitable constants, in terms of any other one, and the theory, as such, might well be said to be complete.

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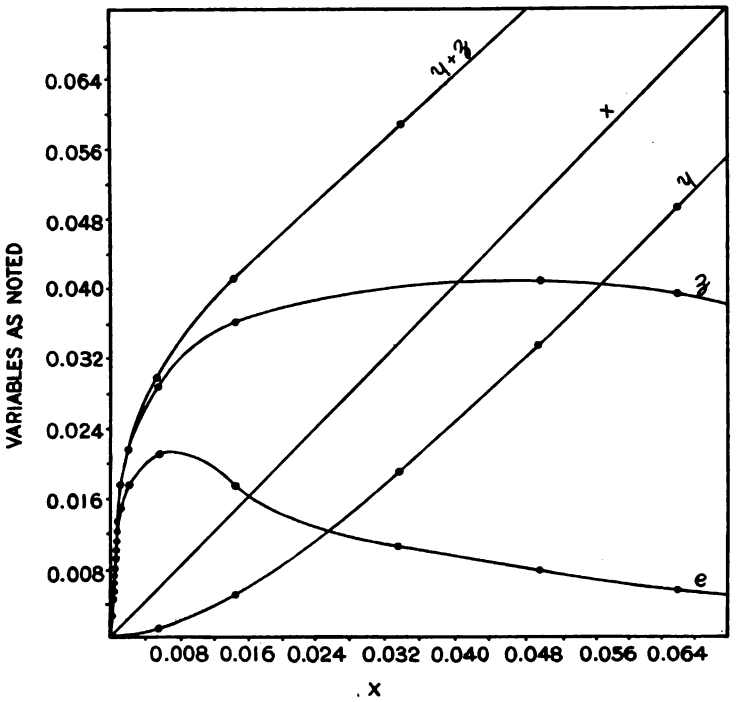
It was conceived that by means of the hydrogen electrode we could determine all the variables in a special experiment in which the volume was kept more nearly constant. One gram of gelatine was dissolved in such a quantity of water that at 33° the volume was 21 cc. This high temperature was used because it is necessary to make hydrion determinations in the melted jelly.

FIG. 4.




The method of using the hydrogen electrode was similar to that used and described by Sörensen (Abstract, this JOURNAL, Vol. 6, pp. 128-55). Acid was added at intervals and the hydrion concentration determined. From the figures obtained it was found possible to calculate all the variables desired. Knowing the quantity of acid added, it was possible to calculate, from the hydrion concentration found, the amount which had combined with the gelatine, and consequently the total concentration of gelatine chloride, giving values for $y$ and $a + z$. Whilst actually there is

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no external solution, there is a theoretical one, since the products of hydrion and chloridion must be equal in both phases; that is, the product $y(y+z)$ of the jelly is equal to the $x^2$ of a theoretical external solution. If, as before, we regard the gelatine chloride as ionized to about the same extent as hydrochloric acid, we can take $K$ as the ionization-constant of hydrochloric acid at a concentration of $a+z$, which is known. From the equation $z(y+z) = Ka$ it follows that:

$$z = \frac{-(K+y) + \sqrt{(K+y)^2 + 4K(a+z)}}{2}$$

in which all terms on the right-hand side are known, and consequently $z$ can be calculated. From $y$ and $z$, also, all other variables can be calculated by formulæ presented earlier in the paper. The results obtained in this way are given in Table II, and are shown graphically in Fig. 4.

TABLE II.

| cc. N/5-HCl added. | Volume produced $V$ | Concentration of acid produced. | Concentration hydrion found. $y$ | Concentration of acid found. | Concentration acid combined. $a+z$ | $z$ | $x$ | $e$ | $y+z$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 21.0 | — | 0.000003 | — | — | — | — | — | — |
| 0.1 | 21.1 | 0.002381 | 0.000006 | 0.000006 | 0.002375 | 0.002351 | 0.000119 | 0.002128 | 0.002357 |
| 0.2 | 21.2 | 0.004762 | 0.000011 | 0.000011 | 0.004751 | 0.004614 | 0.000226 | 0.004202 | 0.004625 |
| 0.3 | 21.3 | 0.007143 | 0.000016 | 0.000016 | 0.007127 | 0.006965 | 0.000334 | 0.006320 | 0.006981 |
| 0.4 | 21.4 | 0.009345 | 0.000030 | 0.000030 | 0.009315 | 0.009064 | 0.000522 | 0.008069 | 0.009094 |
| 0.5 | 21.5 | 0.011628 | 0.000046 | 0.000046 | 0.011582 | 0.011229 | 0.000718 | 0.009817 | 0.011275 |
| 0.6 | 21.6 | 0.013888 | 0.000048 | 0.000048 | 0.013840 | 0.013390 | 0.000803 | 0.011875 | 0.013438 |
| 0.8 | 21.8 | 0.018348 | 0.000117 | 0.000117 | 0.018231 | 0.017665 | 0.001442 | 0.015005 | 0.017782 |
| 1.0 | 22.0 | 0.022727 | 0.000246 | 0.000247 | 0.022480 | 0.021555 | 0.00232 | 0.01741 | 0.021801 |
| 1.4 | 22.4 | 0.031250 | 0.00100 | 0.00101 | 0.03024 | 0.02881 | 0.00559 | 0.02107 | 0.02981 |
| 2.0 | 23.0 | 0.043478 | 0.00501 | 0.00511 | 0.03837 | 0.03621 | 0.01437 | 0.01748 | 0.04122 |
| 3.0 | 24.0 | 0.062500 | 0.0193 | 0.0201 | 0.0424 | 0.03928 | 0.0336 | 0.01059 | 0.0586 |
| 4.0 | 25.0 | 0.080000 | 0.0335 | 0.0350 | 0.0450 | 0.04098 | 0.0500 | 0.00813 | 0.0745 |
| 5.0 | 26.0 | 0.096154 | 0.0492 | 0.0521 | 0.0440 | 0.03935 | 0.0660 | 0.00573 | 0.0886 |

The curve of special interest is that of the variable $e$, which is seen to increase to a maximum at a very low concentration and then to fall in a manner similar to that of the volume curve (Fig. 2). Since $e$ represents the measure of an outward pressure, we have, when the jelly is free to swell, an application of a special case of Hooke's Law, *ut tensio sic vis*, where stress $= c \times$ strain; and since $e$ is a uniform pressure, it follows that it will produce an increase in the size of the jelly, but not in its shape, and that the increase in volume will be directly propor-

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tional to the pull. If we take the volume of 1 gram of dry gelatine as 0.7 cc., then, so long as the elastic limit is not exceeded, $e = k(V - 0.7)$, where the value of the constant is determined by the bulk modulus of the gelatine or particular protein under consideration. The relation is therefore dependent on the temperature, and that this is an appreciable factor is shown by the following rough experiments:

| Initial concentration of acid | Volume of jelly | | |
|---|---|---|---|
| | 7° | 15° | 33° |
| 0.200 | 11.3 | 17.6 | — |
| 0.100 | 13.0 | 19.8 | — |
| 0.050 | 14.6 | 23.2 | 33.0* |
| 0.025 | 18.5 | 27.3 | — |
| 0.010 | 22.2 | 34.3 | — |

* The value for the volume of 33°, a temperature well above the melting point of the jelly, is approximate only, and was obtained by gradually raising the temperature of the swollen jelly and its equilibrium acid, when the jelly, from its gravity and viscosity, does not mix with the supernatant liquid.

It is probable that the effect produced by this limited rise of temperature is not due to material changes in ionization or chemical activity, but almost solely to the diminution of the solid cohesion of the jelly. Many reasons convince us that the cohesive forces of the jelly opposing $e$ are still maintained beyond the melting point.

It is evident that the volume of the jelly, at a constant temperature, is dependent for its value on the value of $e$, and the only remaining question is why the value of $e$ should follow a curve of the particular type that it does. As was noted earlier in the paper, the following equation results from a simultaneous solution of the thermodynamic and osmotic equations given:

$$e = -2x + \sqrt{4x^2 + z^2}.$$

As the concentration of acid is increased from zero to some small, but finite, value, $z$ must necessarily increase at a very much greater rate than $x$. This is shown very markedly in the most dilute solutions, where almost all the acid added combines with the gelatine: but $z$ has a limiting value, which is determined by the total concentration of gelatine with which we started. Now $z$ must either approach this limiting value or diminish, which

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it would do if the ionization of the gelatine chloride were sufficiently repressed. In either case:

$$\lim_{x = \infty} \sqrt{4x^2 - z^2} = \sqrt{4x^2} -$$

from which it follows that:

$$\lim_{x = \infty} e = -2x + 2x = 0.$$

It is clear from this that, as $x$ increases from zero, $e$ must increase to a maximum and then decrease, approaching zero asymptotically, regardless of whether or not the ionization of the gelatine-salt is appreciably repressed. In Fig. 4 it will be seen that $e$ begins to decrease at a considerable rate while $z$ is still increasing slightly, which would be expected. It should be noted that the apparent decrease in $z$ in the most concentrated solution, given in Table II, is due chiefly to the increased volume.

An interesting point is raised here regarding the action of salt in repressing the swelling of jelly swollen with acid. Whilst the salt undoubtedly represses the ionization of the gelatine chloride to some extent, it would scarcely be sufficient to account for the fact that salt reduces the volume of jelly almost to that of dry gelatine. The chief action is probably that the addition of salt corresponds with an increase in the value of $x$, and that this increase in $x$ must, according to the equation just discussed, produce a decrease in the value of $e$, with a corresponding diminution of the volume of the jelly.

## Summary.

When gelatine is immersed in a dilute solution of an acid, combination takes place between the gelatine molecules and the hydrogen ions, resulting in the formation of a highly ionizable salt of gelatine, the anion of which in tending to diffuse exerts on the jelly mass an outward pull, which, being uniform in all directions, produces, according to Hooke's Law, an increase in the volume of the jelly proportional to the magnitude of the pull. In the case of gelatine immersed in a very dilute solution of a highly ionizable acid (say, 1 gram of gelatine in 100 cc. of N/1000 hydrochloric acid) almost all the acid combines with the gelatine, and we have the simplest type of equilibrium, where,

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practically, $x = 0$, $y = 0$, $y + z = z = e$, and the concentration of the anion of the jelly is the measure of the outward pull and consequently of the increase in volume. In more concentrated acid solution (say, 1 gram of gelatine in 100 cc. of N/10 hydrochloric acid) only a part of the acid combines with the jelly, and we have $y + z > z > e$, but here it is neither the total concentration of anion of the jelly nor that of the ionized gelatine-salt which is the measure of the force producing swelling, but it is the excess of concentration of diffusible ions of the jelly over that of the external solution. This quantity $e$ is a direct measure of the swelling so long as the swelling does not exceed the elastic limit, and offers a complete explanation of the peculiar swelling curve obtained by immersing gelatine in increasing concentrations of hydrochloric acid (see Fig. 2). In the most dilute solutions $e$ will increase almost directly with the increasing initial concentration of acid, but will approach a maximum as the formation of the gelatine monochloride nears completion, and must then decrease as $x$ becomes larger, according to the equation $e = -2x + \sqrt{4x^2 + z^2}$, where $z$ has a limiting maximum value. The repression of swelling by the addition of salt is caused by the apparent increase in the value of $x$ produced, which results in a diminution of the value of $e$ and consequently in a repression of the swelling, this action being assisted to some extent by the repression of the ionization of the gelatine-salt.

In the case of weak acids, like acetic, a greater total concentration of the acid is required to produce nearly complete combination of the gelatine with the acid, because the degree of combination is determined by the value of $y$, which, even in the more concentrated solutions, will be small because of the repression of the ionization of the acid by the highly ionizable gelatine-salt. For this reason the swelling of gelatine in acetic acid increases with increasing total concentration of acid, and is not repressed by the addition of an excess; in fact, the swelling continues up to a strength of acid of N/1 beyond which solution of the gelatine takes place. The somewhat stronger formic acid actually shows slight repression, whilst very weak acids, such as boric, as would be expected, produce little, if any, swelling.

In pure water, combination must take place, although probably

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only to a very slight extent, between the gelatine molecules and the hydrion of the slightly dissociated water, leaving in the jelly a corresponding excess of hydroxyl ions which tend to diffuse outward, causing the jelly to swell. The presence of sulphites in the gelatine and carbonic acid in the water tend, of course, to produce a greater swelling than the minimum, which would result from pure gelatine and water, difficult, if possible, to obtain

Some work has been done on the equilibrium of gelatine and alkalies, but solution of the gelatine took place at so low a concentration of the alkali (at about $x = 0.04$ for sodium hydroxide at 20°) that the work could not be carried out to the extent desired. Work on hide has shown that the swelling is repressed either by the addition of excess of alkali or by the addition of ammonium chloride. In the former case the swelling is repressed by the increase in the value of $x$, according to the law derived for acids; in the latter case by bringing the solution back almost to a condition of neutrality, the gelatine compound being again decomposed. It is probable that the laws governing alkaline-swelling are the same as those governing acid-swelling.

It will be seen that the laws discussed are quite general, and that for any particular sample of gelatine at constant temperature any variable can be expressed as a direct function of $x$, and that for all acids the value of $K'$ will be the same, whilst the value of $K$ is merely dependent on the degree of ionization of the gelatine salt formed. With suitable values for $K$, $K'$, and $k$, the laws are probably applicable to any protein and any acid or alkali.

If, as the authors believe, the foregoing theory is not merely applicable to gelatine, but, with appropriate constants to the colloidal swelling of all proteins, it is obviously of far-reaching importance, not merely to the special technology in which it originated, but to many physiological and medical problems. It is only necessary to allude to the work of Loeb on the fertilization of the *Echinus* egg by saline solutions, of Fischer on œdema, and of Pauli and others who attribute muscular energy to colloidal swelling and contraction produced by the alternate action of sarcolactic acid and the saline constituents of the blood; whilst many of the problems of plant-growth and of the semipermeability of vegetable membranes are probably due to analogous causes; and

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the laws which regulate the swelling of carbohydrate jellies, such as agar-agar, starch, and cellulose itself demand a similar investigation.

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## THE SWELLING OF GELATINOUS TISSUES.*

*By H. R. Procter and Donald Burton.*

(Contribution from the Procter International Research Laboratory.)

[EDITOR'S NOTE.—The first part of this paper is an abstract of the paper by Procter and Wilson, immediately preceding, and is therefore omitted.]

Before the principles discussed can be incorporated into any system of control work it will obviously be necessary to perform a number of practical experiments which can probably best be done by the tannery chemist, for whom the problem is simplified by specific requirements and conditions, as well as by having a continuous process upon which to make observations. It is intended to continue the more practical side of the problem in these laboratories later, but it has seemed advisable in the meantime to attempt to arouse the interest of the tanners' chemist in a problem which we hope will be of great importance to him.

At this point the "practical" man will be apt to think that he has been given a lot of abstruse theories and much mathematics complicated with unknown "constants" some of which are not even really constant, and that at least till these are known it is impossible to put the work to any real use. Of course all this is too true, and is inevitable in any investigation of a theory which is at all complicated, for one must know the way in which actions are related before one can begin to determine working constants. It is however much to know on what the relation of one fact to another depends, and even that there is a regular relation at all, and in this sense we believe something useful has been accomplished. We have shown that, other things being equal, the swelling and the amount of acid or alkali absorbed is dependent on the hydrogen ion concentration of the outer solution, while

* *J. S. C. I.*, April 15, 1916, pp. 576–83.

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it is repressed by that of the anion, and for a given chemical compound such as gelatine or the collagen of hide-fiber at a given temperature there will be no difficulty in making tables or curves to show these for any known concentrations. The real trouble

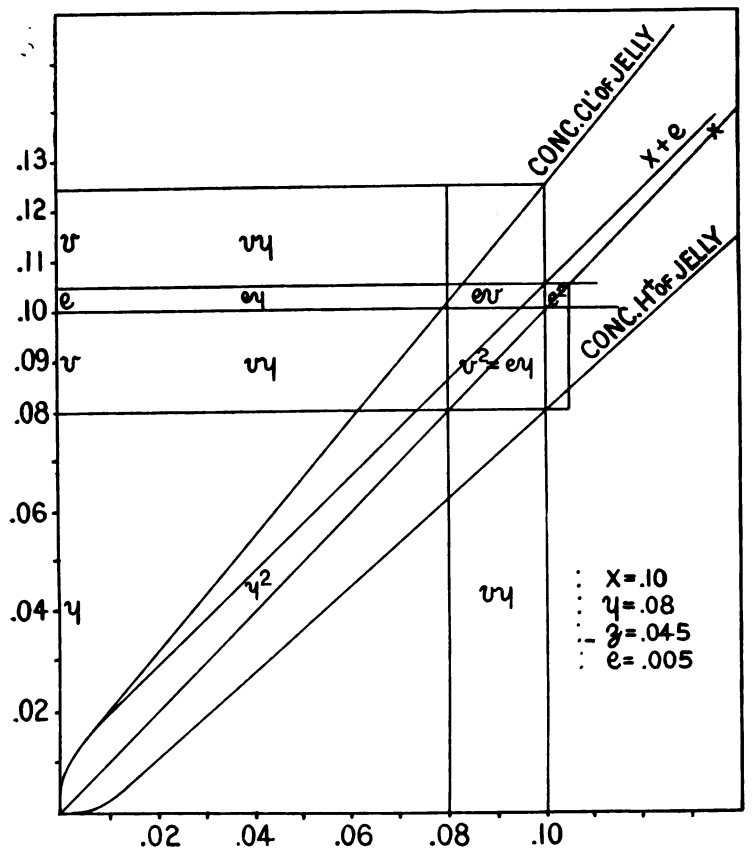


FIG. 1.
Curves OF Concentration.

arises from the solid elasticity of the material which introduces another "constant" which we have called the "bulk-modulus," of the nature of which we yet know very little, but which obviously varies very much with temperature and mechanical texture of the material. For a given kind of hide at a given temperature it is

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no doubt possible to construct a table giving from the known concentrations of the outer solution the volume of swelling and all the other variables, and this, for his own material, is well within the powers of the tannery chemist. To determine the laws of variation of the bulk-modulus and so make the table calculable for *any* temperature and *any* material may also be possible, but much more difficult and probably too complex for general use, but as most tanners work only a limited range of materials at temperatures which can be kept approximately constant, the simpler table will generally meet real requirements.

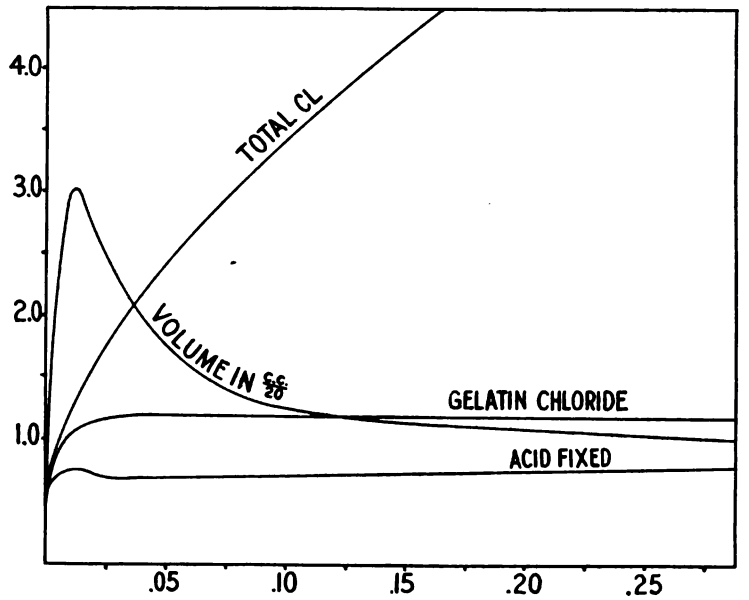


FIG. 2.

Curves of Quantity.
Normality of initial acid.

As to the best method of practical procedure, it may be suggested that graphic curves are in every way better than numerical tables, as in nature almost all changes are continuous, while a table can only give a series of definite steps, and a curve conveys a visual impression of the law of change which a table does not do. To the mathematician the form of the curve often denotes at

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once the nature of the law, and he can say at sight to what sort of algebraical equation it corresponds, but this knowledge is not at all essential to its practical use. No kink in the curve has been observed at the melting point of jellies, and the general form of the curves is completely given in Figs. 1 and 2.

As regards actual methods of determination, the dry weight of hide is best obtained by drying an average sample of the material used, since any attempt actually to dry the pieces used for experiment would materially alter their character.

If the molecular concentration of the acid be determined by titration, as must generally be the case, it must not be forgotten that the equilibrium depends on the ionized part only, and that while this is 90 per cent. or more of the total molecular concentration of strong acids such as hydrochloric or sulphuric, it is a very small fraction of it in weak acids like acetic, so that in comparing experimental curves it must be remembered that the greatest ionic concentrations of weak acids correspond to very small normalities of strong ones.

So long as only pure acids or alkalies exist in the outer solution it is not difficult from tables and published matter to ascertain the actual ionic concentration, but in the jelly the matter is complicated by the repressive action of the highly ionized gelatine-salt on the ionization of the acid or alkali, so that it is usually best to be content with mere normalities, but in this case it must not be forgotten that much larger apparent quantities of free acid in the jelly in proportion to the gelatine-salt will be required for the equilibrium with weak acids and will correspond to no greater hydrion concentration.

In considering outer solutions containing salt it is necessary to remember that the action of the anion is to repress the swelling of the gelatine-salt, while the function of the hydrion is to maintain the quantity of the latter by preventing hydrolysis. As this is almost completely stopped by solutions above 0.05N of hydrion concentration there is little difference in the effect in reducing swelling of further additions of acid or of its neutral salt, except that the latter cannot cause hydrolytic decomposition of the gelatine. Below 0.05N it is necessary to consider the functions of the hydrion and anion separately.

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The determination of the total acid in the jelly or hide includes not merely the free acid but the combined anion of the gelatine-salt which is decomposed by titration with a strong alkali. If the titration is made direct in the hide with sodium hydrate and phenolphthalein, many hours are required to reach the final neutral equilibrium, while methyl-orange fails to estimate the last portions of combined acid. Adopting a suggestion of Mr. J. A. Wilson, the process may be shortened by digesting for some hours with excess of a N/10 solution of sodium bicarbonate and titrating back an aliquot part of the solution. In this case methyl-orange must be used, but for greater accuracy the final titration may be made at a boil with alizarine or litmus as indicator.

It is not possible by direct titration to determine the actual *free* acid in the hide. With jellies and strong acids approximate results may be obtained by salting out as described in a previous paper,[1] but the method is not accurate when applied to weak acids. Under certain conditions the ionic concentration can be directly determined electrometrically by the hydrogen concentration cell, but this has its limitations and requires special apparatus. With strong acids and certain assumptions the free acid concentration can be calculated very approximately from the total acid absorbed by the jelly by the formula:

$$\text{Free acid} = \frac{x^2}{\text{total acid}},$$

where $x$ is the concentration of the outer solution; but with weak acids the necessary corrections for ionization are very complicated.

The following method will give approximate results even with weak acids if the concentration of the outside solution is not too small. A known quantity of the hide-material calculated to dry weight is placed in a known volume of acid of definite strength and allowed to remain with occasional shaking till equilibrium is reached (at least 48 hours). The acid is then poured off into a graduated cylinder and the skin allowed to drain into it for an hour or two in a covered funnel. The volume of swelling is then calculated from the loss of volume of the solution plus the water originally contained in the skin, and an aliquot part of the

[1] *Trans. Chem. Soc.*, 1914, Vol. 105, 316, this J. 1914, p. 210.

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liquid is carefully titrated with sodium hydrate and phenolphthalein to determine the equilibrium concentration. The skin is now treated with excess of common salt and allowed to drain thoroughly and pressed between filter paper to remove as much liquid as possible, and the remaining combined acid titrated in it by one of the methods described above. This will be the combined acid (ionized or not), and deducted from the total acid of the jelly will give the total free acid (ionized or not). The principal source of error is the change in the hydrolysis of the jelly-salt by the minute quantity of free HCl formed by the action of the organic acid of the salt. The organic acid combined with the gelatine is almost wholly and quantitatively replaced by hydrochloric. The ionization may be approximately calculated from known ionization-constants if that of the salt be presumed equal to other salts of the same acid. The results may be to a certain extent checked by division of the (ionized) $x^2$ by the (ionized) total acid, which should equal the (ionized) free acid found.

Proceeding from methods of investigation to the application of the theory to explain actual problems of leather manufacture, its most direct application will be to the process of pickling, to elucidate which the research was originally started. This process consists in outline in treating the skins in an acid bath to form the gelatine-salt, and then in a concentrated common salt solution to repress the swelling and to substitute salt for all or part of the free acid in the skin without removing that actually combined. The acid generally used is sulphuric to which some salt is usually added to moderate the swelling, but any other acid can be substituted which will give the solution of about N/20 of actual hydrion concentration which is required for a practically complete saturation of the gelatine base. In any case if common salt is used to repress the swelling, the acid left combined with the gelatine is almost entirely hydrochloric which is substituted by the salt for the original acid used; skin pickled with formic acid was found by analysis to contain almost 3 per cent. of chlorine reckoned as HCl combined with the gelatine base, and even where sulphuric acid is used the substitution is nearly complete. It may seem strange at first sight that a weak acid should be capable of

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decomposing salt, but it must be remembered that the gelatine-salt is highly ionized and the sodium chloride is present in enormous excess so that according to the mass-law the quantity of gelatine formate remaining must be vanishingly small. The salt acts on the equilibrium by enormously increasing the outside Cl′ pressure without adding to that of the ionizing gelatine chloride so that the free acid is almost completely expelled and the actual fiber nearly dehydrated. Gelatine can be so compressed as to retain less than its own weight of water and an appreciable portion of salt is expelled from this retained solution by the osmotic pressure of the gelatine-chloride.

The pickling process is used both as a means of preserving the skins even for months in a wet condition, and as a preparation for tanning, especially with chrome; and the requirements for the two purposes differ considerably. For mere preservation it is probably desirable to use as little excess of acid as possible beyond that needed to saturate the gelatine base, and to substitute the free absorbed acid entirely with salt solution. In practice, however, mainly to save time, it is found convenient to use stronger acid solutions, which in reasonable limits do not do much harm. Neither the quantity nor the concentration of acid required to produce the best results can be exactly given, as they are dependent not only on the character of the skins but on the volume of the liquor, but about 7.5 grams of concentrated sulphuric acid, and 80 grams of common salt per liter has given good results on sheepskins in such quantity as can be conveniently paddled in it. One hundred cc. of such a solution will require about 15 cc. of N/1 alkali for neutralization, which will be reduced to 8-10 cc. by use, partly through dilution by water brought in by the skins. The sulphuric acid may be replaced for several packs, but the salt will gradually be converted into sodium sulphate which will also control the swelling. The usual method in practice is to put a "jugful" into the vat for each lot of skins, or more if the foreman is so minded, and usually too much is used. The salt solution should always be kept saturated and the skins paddled for at least twenty minutes in it. It is not usually changed and consequently gets more and more charged with acid, and it would no doubt be better from time to time *nearly* to re-

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store its neutrality by addition of soda. Pickled skins swell inordinately if placed in water and hence must either be neutralized or tanned in salted liquors, and of course the more acid is left in the skins the more salt is needed in the tanning liquor. We see no practical object in substituting more expensive acids for sulphuric except to minimize the effects of careless pickling.

When pickling is used as a preliminary to chrome tanning the objects are different and the method must be modified accordingly. In the two-bath process the skins are first brought into a bath of bichromate acidified with hydrochloric or sulphuric acid to liberate chromic acid. Pickled skins carry in with them a certain quantity of acid, so that the acid added directly to the bath must be reduced, and as only free chromic acid is fixed by the skins, they are penetrated rapidly and evenly by the bichromate from which the chromic acid is liberated on the fiber and the acid in the skin is neutralized by its soda or potash base. Probably other purposes are also served by the preliminary swelling. It is thus desired to carry acid in with the skins and the final salt bath is omitted, sufficient salt being added to the acid bath to control the swelling as desired. In considering the acid required it must not be forgotten that the skins mechanically carry an appreciable quantity of the acid solution with them into the chrome bath.

Skins are also frequently pickled as a preliminary to the single-bath process of chrome tanning, but with somewhat different objects. The tanning liquor is a solution of a basic chrome salt, and the more basic it is the greater the quantity of chrome ultimately fixed by the skin. As, however, basic chrome solutions are colloidal, too basic solutions tan the surface too heavily and penetrate very slowly to the center, and bringing the skin in an acid condition into the bath enables a more basic solution to be used without producing this effect.

Pickling is also sometimes used as a preliminary to ordinary vegetable tannage in salted liquors and it is found that soft tannages can be produced in this way in less time and with less tanning material than where the pickling is omitted. The effects of pickling on tannage are no doubt in part at least dependent on the fact that the colloid compound gives rise to a surface electric

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potential on the molecules or their complexes which must have a profound effect on adsorption and colloidal combination, but the study of these electrical phenomena, though begun is yet far from complete. When these problems are solved, it is probable that the vexed question of the necessary acidity of tan liquors can be definitely dealt with. Apart from pickling, and metallic tannages which themselves are in part pickling processes, the theory explains a good deal even with regard to alkaline swelling and the bating and puering processes. It probably offers a complete explanation of the different degrees of swelling produced by different alkalies and alkaline salts, but its application to the theory of bates and puers is still more interesting, if as yet more speculative. If hide is swollen by an alkali such as lime, the swelling is gradually reduced by neutralization, and, with increase of acid, again increases as the skin becomes acid; but it is recognized by the practical manufacturer that the depletion produced by the most careful deliming is less thorough than that obtained by the use of ferments, dung bates or puers. While the acid swelling is due to the acid anion combined with the skin the alkaline is caused by hydroxyl ionized from complex gelatine base formed with the alkali, and the hydroxyl concentration is inversely proportional to the hydrion concentration. At the neutral point of water a certain pressure from the acid anion still exists and the curve of acid swelling is prolonged to the alkaline side of this neutral point while the hydroxyl swelling only takes its origin there. It follows that in a swelling curve compounded of these two curves the minimum point must be, not at the neutrality of water, but somewhere very slightly on the alkaline side. All the dung bates in action are alkaline. It is true that, in a transition from the alkaline to the acid condition, goods must necessarily pass through this point of minimum swelling, but to produce the required effect they must not merely pass through it but be maintained at it for sufficiently long for the effect to be produced; and this can only occur in presence of some base just weak enough to regulate the hydroxyl concentration on the required point. This may be made clear by an illustration. With a strong acid and base a solution may well pass from the acid condition indicated by methyl-orange to the alkaline one of phenolphthalein

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with a single drop of N/10 solution, while in presence of a weak acid many cubic centimeters may be required. Dung bates naturally contain a variety of excessively weak amino-acids and amine salts, and it is not improbable that the mixture may nearly hit the required minimum. Wood has shown[2] that a mixture of an amine salt, and an enzyme to digest the keratin residues and other matters requiring removal will produce the essential effects of a puer; and "Oropon" containing ammonium chloride and pancreatic enzymes is for many purposes a successful substitute, but it is unlikely that in either case the *optimum* alkalinity is exactly attained. The problem of a perfect chemical puer is thus reduced to the search for suitable enzymes and suitable salts of weak bases and does not seem impossible of solution. The hydroxyl concentration of working puer liquors is easily determined by the hydrogen electrode.

In this connection it may be pointed out that though the total alkalinity of old and mellow times is greater than that of fresh ones, it is quite probable that their hydroxyl concentration is lower, because of the dissolved amino-compounds which they contain together with bacterial enzymes As Stiasny has shown the alkaline effect of ammonia present, to which a good deal of the alkalinity is due, is much reduced by its tendency to form complex ions with lime comparable to those which it forms with copper.

Apart from the questions of leather chemistry the theory has important applications. The kindred industries of dyeing and textiles are also based on the behavior of fibers which are in their nature colloid jellies, and though their chemical constitution differs from that of skin; it is almost certain that their behavior is governed by analogous laws.

With animal physiology and medicine the relation is still more direct. It has been shown by Pauli and others that in all probability muscular contraction and relaxation depend on the same causes as govern the behavior of the pickled skin; and Dr. Martin Fischer attributes the dropsical swelling of kidney and ovarian disease and the failure of blood pressure in "surgical shock" to acid swelling of the tissues which he treats with salt and alkalies.

[2] *J. S. C. I.*, 1898, 17, pages 1010 to 1013.

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Probably Loeb's fertilization of star-fish eggs by salt solutions is in the same connection.

## NOTE TO THE EDITOR.

The difference in action between acids and alkalies in the swelling and contracting of gelatine and hide-substance may be expressed as follows:

$$(HOOC)_m R(NH_2)_n + n H^+ \boxed{+ \underset{n}{Cl'}} \rightleftharpoons (HOOC)_m R(NH_3)_n^{n+} \boxed{+ n Cl'}$$

$$(HOOC)_m R(NH_2)_n \boxed{+ m \overset{+}{\underset{-}{Na}}} + m OH' \rightleftharpoons m H_2O \boxed{+ m \overset{+}{\underset{-}{Na}}} + (OOC)_m R (NH_2)_n^{m\theta}$$

where R represents the remaining portion of the gelatine molecule. Gelatine chloride is formed by the *combination* of gelatine and HCl, while sodium gelatinate is formed by *neutralization* of some of the carboxyl groups of the gelatine by NaOH. In the first case the concentration of gelatine ion will become nil only at $[H^+] = 0$, in the case of alkaline swelling the gelatinate ion becomes nil at the neutral point, where $[H^+] = 10^{-6.9}$. Therefore the point of *minimum* swelling must lie between $[H^+] = 10^{-6.9}$ and $[H^+] = 0$, or somewhere on the alkaline side, and because of the great degree of swelling produced by dilute solutions of strong alkalies, this point must lie only slightly to the alkaline side of the neutral point.

All increases in concentration of gelatine ions (or gelatinate ions) tend to increase the volume of the jelly, while the addition of any electrolyte not increasing the concentration of colloid ions must repress the swelling of the jelly according to the concentration of added ions. The repression of swelling is produced, not by any particular kind of ion, but solely by a diminution of the total difference of concentration of diffusible ions of the two phases.

J. A. W.

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## FELLMONGERING AND TANNING SHEEPSKINS IN NEW SOUTH WALES.

*By F. A. Coombs, E. Swinbourne, and G. W. Gabb.*

In the New South Wales fellmongering industry sheepskins are usually described as merino or cross-bred, the former denoting fine and the latter coarse wooled skins which include pure-bred Lincoln and Leicester. The pelts from fine wooled skins are usually thin, with an open and irregular grain, and the pure-bred merinos, particularly the Vermonts, are covered with ridges on the grain side; such skins are usually called ribbies. These faults affect the quality of the resulting leather, and the pelts from fine wooled skins are usually only fit for the production of low grade leather. The pelts from coarse-wooled skins are usually stouter, and not so open, but more regular in the external features of the grain than those from fine wooled skins, and therefore the former can be used for the production of higher grades of leather.

Pelts vary considerably in area, substance, and external features of the grain, the variations being largely due to difference in age, breed, health of the animal, amount of wool on the skin, and to climatic conditions. The pelt begins to fill up and get stouter after the wool is shorn off the sheep. A skin with "good substance" might be described as being thick, and the internal growth of white fibers would be dense, which means a greater concentration of the leather-producing constituents of the pelt.

Australian squatters have been breeding merino sheep for a high class wool. These sheep are particularly hardy when exposed to changes common to a dry, semi-tropical climate, and therefore thrive well in Australia; but the merino pelt is poor, and fellmongers and tanners are agreed in the opinion that the sheep pelts of Australia, merino predominating, are not worth the amount of skilled labor that can be profitably employed on pelts from coarse-wooled skins.

In New Zealand the merino has been practically ousted by the more profitable cross-bred sheep, which give such good results in the frozen mutton trade, and at the present time the proportion of cross-bred sheep is increasing in Australia, and tanners already note a decided improvement in the pelts. The merino sheep produce the finest wool and the worst pelt, the wool generally re-

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turning considerably more money than the pelt. This difference in relative values reaches the maximum in long wooled merino skins, and the minimum in short coarse wooled skins (shorelings) taken from the animal just after the sheep has been shorn; but while the pelt of a coarse wooled shoreling is worth more than the wool, the number of these skins is proportionately small, and therefore the wool is the more important product in nearly all fellmongering centers.

Fellmongering is that process which involves the separation of wool and pelt, and for sheepskins is similar to the methods employed by the tanner for removing the hairs from various skins; but the tanner does not consider the hair when treating the hair skin, and unfortunately some fellmongers do not consider the pelt when treating wooled skins. However, the difference between the preparatory treatment of sheepskins and calfskins will not be found in the materials used, but more in the method of using them. For dehairing purposes, calfskins are immersed in solutions of alkaline sulphides and lime, but the same treatment would destroy the wool on sheepskins; therefore, when this method is used, the latter are painted on the flesh side with the sulphide mixture. But in New South Wales approximately all the skins are dewooled by the sweating process, and a great number of pelts are lost each year which would be saved under a chemical process.

The first process at the fellmongery or tannery is soaking. The skins are placed in large water vats and washed free from dung, dirt, and blood. The time allowed for this soaking depends entirely on the condition of the raw material. Fresh butcher's skins give the least trouble in the soaks; but the dry or dry salt-cured skins remain for a longer period, to allow the pelts to take up water and come back to that soft pliable state peculiar to the pelt of the fresh green skin. The soaks, which contain a number of putrefactive bacteria, are not sterilized by the fellmonger, and the green skins should not remain here more than twelve hours. It is the usual practice to have all the skins in the soak pits within twelve hours after they have been taken off the animal. Failing this, they should be treated with the object of preventing or delaying bacterial action, which is not desirable at this stage, because it would be uncontrollable; but unfortun-

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ately a great number of pelts are thus destroyed. The wool contains large numbers of putrefactive bacteria; and when the skins are passing from the butcher to the fellmonger, the inner, or flesh side, is exposed to the air and brushed by the wool, becoming inoculated with bacteria on a part of the skin which at this stage is often covered with blood, and is therefore an ideal medium for their growth, especially if the temperature of the fresh warm skin is not brought within reasonable bounds by allowing what the trade call the "animal heat" to escape.

Many examples could be given illustrating the damage done to all classes of skins, hides, and fur skins, by putrefactive bacteria attacking the material before it reaches the tanner or fellmonger, and it is a common sight to see parts of a skin completely destroyed, while other parts are perfectly sound.

Mechanical and chemical agents, by bruising and penetration, enable the dry pelt to take up water more quickly than would otherwise be the case; but the results from any softening process depend almost entirely on the method of curing the skin for the raw skin market. It will be readily understood that when a hygroscopic substance like common salt is used for curing skins the softening process will give less trouble. When salt is placed on the skin, it withdraws moisture from the pelt, and a portion of the salt is dissolved and retained by the water that still remains in the pelt. The skin is now dried out to a state called dry-salted, and the salt remains in the pelt. Any skin that is worth drying out for its pelt value is worth salting. Sheepskins that have to be railed to the market, or even held up for a few days for the sales, are always dried out without the addition of salt. An important condition when soaking dry skins is the temperature at which they are dried out, and this is not controlled by the tanner or fellmonger. Skins dried on fences, etc., at a high temperature by exposure to sun are useless for producing a leather of average quality, but if the drying be carried out at a low temperature good results can be obtained by the tanner. Collectors who wish to get the maximum market value for fur-skins, etc., should use salt on the green skins, and then dry them out at a low temperature.

After soaking, the skins pass through the burring machine, which removes a large amount of dirt and seeds from the wool, and when the skins are put in, flesh side up, the mechanical action

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assists to bring the dry skins back to their original pliable condition. The skins are sprayed with water when they are passing through the burring machine; and when the rollers are reversed, the skin comes out freed from all surplus water, and in a condition suitable for either sweating or painting.

The skins are removed, after burring, to the sweat house, where they are suspended on hooks and exposed under conditions favorable for the action of bacteria. This process, called sweating, aims at a result which may be described as a partial decomposition of the skin, and the end point is reached when the wool or hair can be removed from the skin by the puller. The decomposition required is the result of bacterial action on the epithelium cells of the epidermis, including the hair follicles and the roots of the hair or wool. After noting the histological structure of the skin, one can readily understand that any action, chemical or bacterial, which is capable of destroying the connective links, and breaking down epithelial cells, must leave the wool in such a state that it can be easily removed by the puller. Sections of the epidermis usually adhere to the roots of the wool, when the latter is pulled out of the pelt, so that it does not appear necessary for the cells to be decomposed, but it is rather a case of decomposing or rupturing that tissue which connects cell with cell, or the first layer of columnar epithelial cells to the papillary layer. If the wool be carefully removed from the pelt, the epidermis is seen adhering to the pelt as a white pasty mass of cells which have lost their original strong cohesive properties, and can be scraped off the pelt with one's finger nail.

Bacterial action is not confined to the epidermis; the fibrous tissue of the pelt is also decomposed, but the action is much more rapid on the former than on the latter. If the bacterial action proceeds at a uniform rate all over the skins, the results are good; but if it is patchy, the grain and fibrous tissue will be destroyed before the wool will pull freely from the less favored patches. The weak point in the sweating process is that the bacterial action connected with it is difficult to control, a great number of pelts being damaged, and in some cases completely destroyed. As the action proceeds there is a corresponding rise in temperature, which becomes exceedingly dangerous if it is not controlled. Our local method for doing this leaves room for

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considerable improvement. When the temperature reaches the danger point, trap doors are opened on the top of the sweat house, and the hot moist ammoniacal vapor escapes, and is replaced by air which may be cold or hot according to atmospheric conditions. If the air be cold the temperature of the sweat house decreases, but if the hot dry westerly winds prevail the temperature is not lowered, and under present conditions some of the fellmongers have to choose between opening the trap doors and admitting dry air at a temperature of 90° F., which will dry the skins, or keeping the trap doors shut and finishing the sweating at a very high temperature. In Europe and America water is sprayed over the walls and floor to assist in the control, and we think that if the hot dry air were passed through sprays of water before admitting it through the floor of the sweat house, better results would follow during the hot season, by increasing the humidity and decreasing the temperature.

Given a first class sweating house, much trouble can occur when the skins are hung too close together, owing to imperfect circulation of air. During the sweating process a large amount of ammonia is produced at the expense of the various protein constituents of the skin. The ammonia certainly assists in the dewooling process, and Procter[1] states that ammoniacal vapors alone are capable of reducing a skin to that stage where the wool can be removed from the pelt. The temperature of local sweat houses ranges from 18° to 26° C. (66° to 79° F.), and the humidity is always over 90 per cent. Villon states that 20° to 25° C. is a suitable temperature. He isolated a special micro-organism which he called *Bacterium pilline,* and states that it is aerobic, lives in the presence of various of the putrefactive organisms, and is chiefly concerned in the fermentation peculiar to the process of sweating.

Wood also examined bacteria from the roots of wool in a sweating store, and isolated several organisms, among which are the bacteria described in a paper in *J. S. C. I.* (1899, p. 990) as bacillus D and E, which separately have very little action on the skin, whereas mixed, and working together, the action is rapid and effective.

Pathological changes in the skins often interfere with suc-

[1] Principles of Leather Manufacture, p. 120.

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cessful sweating. If a portion of a skin were to show signs of inflammation without any open sore, one would expect uneven sweating, and in some cases probably a rupture or hole follows on the grain side of the pelt. Skin affections may be due to the fact that the food supplies of sheep are liable to undergo many changes. One month a drought is on, and the sheep are nearly starving, and the next month a good rainfall is followed by a bountiful supply of grass; or as in New Zealand, where the sheep in the winter are often fed on rape and turnips, and according to Seymour Jones[2] the rape has overheating properties. Another cause is the damage done to sheep when they are shipped by rail to certain centers in trucks. The sheep are bruised and overheated, and patches of the skin are often saturated with urine.

Painting is generally considered to be an easier process to control than sweating. Sodium, potassium, and calcium hydroxides are supposed to attack those constituents of the skin which effectively hold the wool or hair in its place; but under ordinary sterile conditions, and at normal temperatures, these substances do not give satisfaction as dewooling agents. Lamb[3] describes an English process carried out by painting the skins with a paint of slaked lime and then placing them in a sweat house for bacterial action to complete the work. To sweat and paint skins would mean a decided increase in labor costs, and the process does not appear to give compensating results. In Australasia the fellmongers either paint or sweat, and the mixed process is practically unknown.

In New Zealand the majority of fellmongers paint their skins with a solution made from sodium sulphide and lime. This is a simple process, and is not affected by the use of sterilizing agents used to preserve the pelt during the soaking period, etc. For this process soaking is carried out in the same way as for sweating, and the skins are put through burring machines and trimmed, then placed in a heap, flesh side up, and painted, using a brush of vegetable fiber.

Procter[4] states that a 25 per cent. solution of sodium sulphide

[2] The Sheep and its skin, p. 209.

[3] Journal of the Leads University Textile Students' Association.

[4] Manufacture of Leather (Procter).

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crystals thickened with lime will give a satisfactory result. Lamb thinks that a 20 per cent. solution should seldom be exceeded, and his ideal mixture for all classes of skins is made up in the following proportions: 60 pounds unslaked lime, 25 pounds sodium sulphide crystals, and 20 gallons of water. This is practically a 12½ per cent. solution thickened with lime. Seymour Jones recommends a mixture of 25 to 30 per cent. on the weight of the rock lime, and the whole reduced with water to the consistency of paint.

Lamb has been getting good results 12 hours after painting by using a weaker mixture containing approximately 10 ounces of concentrated sodium sulphide per gallon, but the strength is probably not the most important factor in the removal of wool from the pelt; but what is of more importance is the amount of water and sodium sulphide on any single skin, and such amounts vary with the workmen and methods of painting the skin; therefore, one might get better results with a thick coat of a weak solution than with a thin coat of a strong solution. Fellmongers sometimes use a strong solution for painting the back or greasy section, and a weak solution for the rest of the skin, but as a rule the skins are painted with only one solution, the greasy backs receiving an excess of paint, which means an excess of sodium sulphide and water. The fellmonger should aim at supplying the skin with just sufficient to give the required result. Any excess will not improve but may have a destructive action on the pelt. Lambskins should be painted with weaker solutions. The early butchers' skins (suckers) will only require about 5 ounces of sodium sulphide (conc.) per gallon. A sodium sulphide paint will always contain caustic soda, which is capable of swelling the pelt considerably above the normal condition, and tender lambs' pelts, if they be exposed to the action of a strong solution, are excessively swollen. A mixture of lime and arsenic sulphide will produce a paint that gives excellent results as a dewooling agent. This paint is quite free from caustic soda, and in some cases, *e. g.*, with tender lambskins, will give better results than sodium sulphide paint.

Procter has suggested[5] a sodium sulphide paint that differs from what has been described by the addition of calcium chloride

[5] Journal of the Leads University Textile Students' Association.

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to remove sodium hydroxide from the paint solution, and states that the following are the correct proportions to employ: 60 pounds lime, 25 pounds sodium sulphide, 12.5 pounds calcium chloride, 20 gallons water. Calcium chloride is used in the Argentine, but appears to be entirely new to Australasian fellmongers.

Procter was the first to point out the probable reaction between the lime and sodium sulphide, resulting in the formation of caustic soda; and Blockey and Mehd, after carrying out experimental work, give the following equation, as showing the probable reaction between portions of these two substances when the proportion of sodium sulphide to lime does not reach higher than one of sulphide to two of lime:

$$Ca(OH)_2 + Na_2S + H_2O = Ca(OH)SH + 2NaOH.$$

Blockey and Mehd[6] also show that when sodium sulphide is added to a saturated solution of lime certain reactions take place, and the amount of calcium left in solution is lower than the amount in a saturated solution of lime water. They also show that the solubility of the calcium compounds decreases as the concentration of the sodium sulphide increases.

The amount of calcium compounds found when N/5 sodium sulphide is made up with a saturated lime solution is so small that apparently only a small portion of the sodium sulphide in these paint mixtures reacts with the lime, and the amount of calcium hydroxysulphydrate formed is decidedly low.

We carried out several experiments by painting one half of a skin with a 10 per cent. sodium sulphide solution thickened with lime; the other half was painted with a 10 per cent. solution thickened with kaolin. Three tests were carried out, and the lime paint proved to be the better in each case. Dry skins were used and the wool did not pull easily, but the lime and sulphide gave distinctly better results. Further tests were tried for comparative results between lime and sodium sulphide, kaolin and sodium sulphide, and kaolin, sodium sulphide and sodium hydroxide, and the results obtained were as follows: No. 1 10 per cent. sodium sulphide, thickened with lime, gave the best results; No. 2, 10 per cent. sodium sulphide, 5 per cent. sodium hydroxide,

[6] *J. S. C. I.*, 1912, p. 369. This Journal, 1912, p. 358.

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thickened with kaolin, was slightly inferior; No. 3, 10 per cent. sodium sulphide, thickened with kaolin, was inferior to both.

Sodium hydroxide was added to the kaolin paint (No. 2), and we thought that such an addition would replace the soluble calcium hydroxide in the lime paint, and give improved results. The results obtained after using No. 2 paint give the impression that further experiments in this direction may lead to the exclusion of lime from painting mixtures, and this would mean a skin wool absolutely free from lime.

Paint solution No. 3 should be an ideal mixture for lamb and light skins, and the amount of sodium sulphide should be adjusted to suit the age and substance of the skins. The addition of sodium hydroxide to the above painting solutions did not adversely affect the few pelts in our experiment, but we recognize that more experimental work is necessary.

The wool is generally, but not always, the more important product in fellmongering, the pelt taking second place, the exception being the short-wool skins, especially those from sheep other than merino. The various processes for the removal of wool may all adversely affect its quality. We have considered the pelt first, because any method for dewooling is based on methods capable of decomposing certain of its constituents.

Wool from fellmongered skins is usually known as skin wool, and apparently various writers differ as to the fellmongering process which gives the best results from the standpoint of the quality of the wool. One English scientific wool expert[7] states "that the sodium sulphide process is the best, as this agent has no influence on the wool fiber," and with the sweating process he states "that there is danger that the wool fat and yolk may be extracted from the fiber, leaving it lean, tender, and wasty; but in Mazamet, in France, where the sweating is well understood, wools of excellent color and quality are available after passing through this sweating process." Part of this statement practically admits that under skilled control the sweating process returns good results.

Seymour Jones[8] states that in Mazamet 25,000,000 woolskins are fellmongered annually, and sweating is largely carried on,

[7] The Wool Year Book, 1911, compiled by A. F. Barker. M. Sc.

[8] The Sheep and its Skin, p. 274.

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but the fellmongers are gradually turning their attention to the milk of lime and sodium sulphide process, because of the simplicity of the operation, less cost, and improvement in wool and pelt. He also states that the sweating process is good for the wool, but is objectionable on account of the injury it causes to the pelt. Lamb[9] writes that from the standpoint of the condition of the wool, the sweating process is one of the best.

In New South Wales the majority of the fellmongers and wool-buyers consider that sweating is superior to the chemical or painting process, so far as merino wool is concerned. The fine merino wools are used for the manufacture of the best woolen materials, and it is claimed that the wool from sweated skins is brighter, has a better color, and gives better results after dyeing than wool from painted skins.

We quote an expert who states that sweated wool is liable to become tender, owing to the removal of fat and yolk from the fiber, and there is no doubt that excessive sweating at high temperatures in ammoniacal watery vapor, in the presence of a great number of various bacteria, would decompose those natural lubricants on and in the wool fiber, and would probably attack and slowly decompose some of the protein constituents of the wool fiber.

There is a theory which claims that if all the fat and yolk are removed from the fiber, the tensile strength of the wool is lowered, and any application of oil will not bring it back to its original condition; and we must consider the possibility of sweated wool reaching this undesirable stage. In New South Wales we have a number of men who have had considerable experience in the sale of wool from sweated skins, and they state that the same buyers come year after year and buy this class of wool, so that we have a certain amount of proof that it is not tender, but only careful experiments would show if it had been adversely affected by the process of sweating.

Bacteria are capable of decomposing hair keratin, but the action is decidedly slow under normal conditions. Pieces of trimmings off wooled skins are sometimes sweated in heaps, and as such a method is difficult to control, the material is often over-sweated, and the resulting wool is a bad color, while the quality is ad-

[9] Journal of the Leeds University Textile Students' Association.

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versely affected, as is usually noted by the lifeless "feel" when handled by the expert. In some cases the keratinous structure of the wool fiber is attacked in such a manner as to affect its quality, but even in the extreme cases of over-sweating, when the pelts are destroyed, we have never heard that the wool has been affected; so that we can say that sweating skins, as carried out in New South Wales, returns a wool which shows no variation in quality and price corresponding with the variations in the sweating process. As variations are known to exist in the sweat house, we must assume for the present that there is no relation between the quality and selling price of the wool and the process of sweating; but before this sweating process can be described as free from any injurious action, the wool must be followed through the various processes of manufacturing the woollen goods, when research work would show any relation between sweating and such properties as the tensile strength, felting, affinity for dyes, and the ability to give full, bright, clean colors, etc.

Some wool-buyers in New South Wales say that wool from painted skins always contains lime. All the buyers of skin-wool will apparently buy sweated wool, but quite a number, especially of foreign buyers, refuse to touch wool from painted skins. Here again we can find no direct evidence that the best process of painting under experienced control has any effect on the quality of the wool. The old English process of painting with lime only, and then sweating, means frequent handling, especially when flooding with water after painting; and one can easily grasp the fact that the wool on these skins is liable to receive a fair sprinkling of lime, which is probably capable of injuring the fibers, and will certainly give trouble during the process of scouring. There is no doubt that a large amount of skin wool from painted skins contains lime, and buyers are inclined to place this defect as common to all skin wools from painted skins.

Taking the lime and sodium sulphide process as the best example of painting mixtures, we will compare the resulting wool, after painting, with sweated wool. In all painting processes a certain amount of the painting mixture will get on the wool around the edge of the skin; but with skilled workmen the amount at any time is very small, and only on the inferior portion of the wool. Any wool splashed with paint should be thrown aside by

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the puller, or it will be the medium for introducing insoluble calcium soaps into the scouring vats. Leaving out the wool that is splashed with lime, we must consider what is the action of the sodium and calcium compounds in the paint after they penetrate the skin and attack the epithelium cells of the epidermis, hair follicle, and roots of the wool fibers. When the wool is pulled from painted skins, the roots are always alkaline, and this alkalinity shows that certain constituents of the painting solutions are retained by the roots of the wool fibers after the wool is removed from the pelt. Even the lime and arsenic sulphide paints show this alkalinity, and whenever lime is used in the paint it is reasonable to suppose that small portions of a soluble calcium compound will be left on the roots of the wool. Now there is not the slightest doubt that, during the process of scouring, wools from painted skins require more soap than wools from sweated skins.

The favorable factors in the sweating process are: (1) the skins are exposed for a longer time in the wet state from soak to pulling beam; (2) during this time the wool is covered with a mass of mixed bacteria which are capable of decomposing the fatty matters in it; (3) the sweat houses are maintained at a temperature above normal, the humidity is always high, and the skins give off a considerable amount of ammonia, so that one might say they are finished in a weak ammoniacal vapor. Hence the scouring of sweated wool is more economical as regards time and consumption of soap and alkali.

Point to be considered in connection with the painting process are: (1) A great number of pieces are always made, because it is impossible to paint the narrow strips of skin from the legs, and also the thick fleshy parts around the ears, which are cut off and sweated. (2) For a quick and regular turn-over, the advantage lies with the painting process; it is much easier to control, and if one paints skins at night, it is a sure thing that they will pull in the morning. When the skins to be sweated are hung up in the sweat house, one is never sure, under local conditions, when it will "pull." (3) The painting process gives the better pelt. (4) Under present conditions, and taking piece wool into consideration, it would appear as if the sweating process gives the

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best returns, so far as wool is concerned; but, as we have shown, good authorities differ on this question, and we are inclined to think that the best possible painting process in view would not affect the quality of the wool. (5) From a sanitary standpoint painting is the better process, and if some cheap chemical method could be brought into practical existence, to deal with the dewooling of pieces, the painting process would be an ideal one, especially in those freezing works which fellmonger their own skins. (6) Labor costs must vary in different countries, but under local conditions we would expect painting to be slightly dearer than sweating.

The painted wool will certainly require an excess of soap if it contains portions splashed with lime, but if these are picked out, it is improbable that the lime penetrates the skin and fixes on the roots of the wool fiber in sufficient quantity to prove troublesome during the process of scouring. We have experimented with painting solutions which contain no lime, and hope to carry out further investigations on this work.

The men pulling the wool from the skins usually pick out the wool affected by tar brands, etc., also the hair; and the rest of the wool from each skin is usually divided into two qualities, first and second grades, the second grade consisting of burry wool from bellies and flanks. The skins are sorted before they go to the pullers, and the number of classes of wool varies considerably according to the judgment of the fellmonger, but broadly they make combing, clothing, and cross-bred of various qualities.

One interesting point about skin wool is that the whole of the wool fiber is saved, while with the fleece wool, a small proportion is left on the skin; it has been stated that skin wool losses are higher than fleece wool during the process of manufacturing woolen goods.

The wool is usually taken straight from the pullers' beams to the scouring machines. The scouring of the skin wool is done by a machine usually containing three bowls, or it may be described as three machines placed one in front of the other with heavy rollers between for wringing purposes. The common method does not include a steeping bath for the removal of soluble substances, such as the potash salts, which would be washed out when the skins were soaked for fellmongering. The

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skin wool goes without any delay to the first bowl, which contains the "scour," usually made up with an alkaline soap and sodium carbonate. The mode of propelling the wool through the water varies according to the theory of the man in charge of the scouring operations. Some machines have the forks all moving like a harrow, and the wool is pushed forward, while other machines have forks which work alternately one into the other. The object is to push the wool slowly forward to the end of the bowl when it passes through the rollers at the head of the first bowl, and drops into the second bowl, which also contains a certain amount of scour, when the same mechanical work goes on and the wool passes into the third bowl, which contains clean water, sometimes hot, and then it passes through rollers to the drying machine; or, as in a number of fellmongeries, a good portion of the drying is done on the green.

The scour is usually made up with a soda soap containing free alkali, with a further addition of sodium carbonate. Potash soap and potassium carbonate are not in general use at the local wool-scouring factories, and while the theory is that potash scours are better than soda scours, the results obtained from the latter appear to give general satisfaction. However, this could only be settled by bringing our local wool-scourers into closer touch with those who handle and manufacture the wool into woolen goods, and the wool-scouring industry would be placed on a more solid foundation if practical research work were carried out in conjunction with some English experts to prepare a standard method of scouring. The majority of the wool-scourers are good practical men, and good judges of wool; but the industry just lacks that scientific touch which, combined with practical experience, means solidity.

After the wool is pulled off the sweated skin, the pelts are removed with as little delay as possible and placed in lime water with a large excess of lime—about 1 to 2 pounds in 10 gallons of water. In some cases they are washed in clean water, and then they go into the lime vats, which are sometimes fitted with a tanner's paddle, to keep them in motion. These lime liquors are not sterile to all species of bacteria, but apparently they retard the action of those bacteria peculiar to the sweating process. At this stage a great number of fellmongers sell their pelts to the

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basil-tanner, and this preliminary lining in paddle vats is necessary after sweating, or the skins would soon be destroyed by the putrefactive bacteria. This liming process may only last from one to six hours, and the skins are then removed and placed in heaps, where they remain until they are sent to the tannery; or they may be left for three or four days in lime pits, and in some cases two or three weeks. Prolonged agitation in a paddle vat is not desirable, as the continual friction between the pelts and undissolved lime is liable to injure the grain of the pelt.

The real liming process only starts at the tannery and here the pelts remain in lime liquor, without agitation, for four to eight days; when the temperature is low (winter), the skins receive one day extra in the lime. The usual method is to add fresh lime to an old lime liquor and then throw in the skins. Each day the skins are lifted, and the lime liquors are thoroughly agitated, and the skins go back to these liquors before the undissolved lime settles, so that a light sprinkling of lime is deposited on all the skins. The supplies of pelts are so irregular that any organized system of liming, such as the "three pit system" of working from an old lime to a new one, is in direct opposition to the chief aim of the managers of these basil-tanneries, and that is a "quick turn-over"; so that when a rush is on these tanneries are overloaded with pelts, and the method of liming must be one to meet the congested state of the lime-yard, by sharpening up the old limes until they contain an excess of dirt and calcium carbonate. The are then cleaned out, and fresh limes made up with about three parts clean water and one part old lime liquor. This mellowing new lime with old lime liquor is rather the exception than the rule. Approximately the consumption of lime works out at 200 pounds per 1,000 skins.

After the pelts have been in the lime liquors for a few hours they begin to swell or plump, and to reach this state the surface of the pelt must naturally decrease; so that well limed skins are usually drawn, and much stouter than the pelts in their normal state. The theory of the liming process is very complicated, but the practical tanner knows that if the pelts are not limed the resulting leather is hard and thin, and a well limed pelt gives a soft and stout leather. It is generally recognized that, chemically, the lime has a slow decomposing action on the protein

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molecular aggregates, and there appears to be an unstable chemical combination between the lime and certain groups in the protein molecules. This lime and skin-protein compound has a greater affinity for water than the skin-protein, and the natural result follows; the pelt absorbs more water and swells, as explained above. When the pelt swells, a number of cells are ruptured, and the bundles of white fibers are changed in such a manner that the individual fibers are separated and no longer exist as one compact mass. This is essential to the production of a soft leather, and is probably brought about as much by the decomposing action of lime on the cementing substance as the straining and rupturing action of the swollen pelt.

After liming, the skins are thrown up in heaps, and in this condition a considerable amount of water drains away, and varying amounts of the lime are changed to carbonate. After these changes the pelts are not so slippery or greasy to the hand or to the rollers of the fleshing machine, and consequently the workmen are able to flesh a greater number of skins per day. Three or four days are allowed for the skins to drain, but when the busy season is on the skins often remain in heaps for two or three weeks. Lifting the pelts from the lime liquors and placing them in heaps probably only slightly retards the action of the lime on the pelt protein, and pelts should not be exposed in this way for more than three or four days.

Probably the most popular fleshing machine is the Whitney. Here we have the usual cylinder with spiral knives, revolving at a high speed. The pelts are thrown on revolving rollers controlled by the workman's foot; the rollers lift the skin and hold it firmly against the cylinder, and the skin works out to the operator. Only one half of the skin is fleshed at first, and the skin must be turned and the operation carried out a second time before it is completely fleshed. The unfleshed pelts, with butts all one way, are placed close to the operator, who takes each one singly, places it on the rollers, turns it, and then throws it on the heap for the trimmers, never taking his hands off until it is finished. We have seen one man flesh 1,800 to 2,300 sweated, well-limed and thoroughly drained skins in a day of 8¾ working hours.

As far as Australasia is concerned, New Zealand is the home of painted pelts; and while they have as raw material the best

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sheep pelts in the world, the treatment is faulty and leaves room for considerable improvement. New Zealand fellmongers must recognize that before they get the full market value for their pelts the standard of treatment must be raised, not so much by the individual freezing works or fellmongery, but rather by a united effort, keeping in view the fact that if a poor class of pelt were exported from, say, Southland, it affects the market value of those exported from Auckland. The chief faults are probably due to men controlling the painting, liming, etc., who have had no experience in the work of converting the pelts to the various leathers. If one does not see the results of painting, liming, etc., on the finished leather, then one falls short of the ideal practical experience. If one were to take green New Zealand sheepskins, paint, wash, and pickle them, they would then be in a condition to be exported as pickled pelts, and they would look all right, but perhaps to the experienced man they would feel a bit flat. When they are tanned the resulting leather is often hard and flat, or what the trade calls "tinny." Here the trouble is one of liming, and our experience is that a great number of New Zealand pelts are not thoroughly limed. It has been the practice in a number of cases to take the pelts after pulling, to wash, and then throw them into a pit with a little lime, and in some cases without any. Where no lime is used, the liquor becomes alkaline, owing to a certain amount of lime and sodium hydroxide bleeding from the pelts; and if the pelts remain long enough here, they are to a certain extent limed, but it is exceedingly hard to control such a method, and the results obtained are bad. The placing of these pelts in lime pits is too often looked upon merely as storing them, when the rush is on and the fleshing machines are blocked. In other cases liming is secondary to fleshing and getting the pelts in the sacks for export. A great number of New Zealand pelts have been shipped without ever being placed in a decent lime, and while we must admit that painted pelts, strongly alkaline with lime and sodium sulphide, and taking, say, five to ten days to get to the pickle, may reach the physical condition of limed goods without ever going into a lime, the process is too uncertain to give regular results. At the present time, tanners using New Zealand pelts for chrome and white leather do get casks of pelts which give the tinny leather already described, and they are likely

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to get these results until the New Zealand pelts are worked by a standard method based on their leather-producing properties. The sweated pelts, after being trimmed and fleshed, are treated for the removal of lime, which exists as calcium hydroxide combined with skin protein, and varying amounts of carbonate fixed on the fibers and grain. The pelts, after a thorough washing in a paddle with a constant overflow of cold water for about 20 minutes to 1 hour, receive the same treatment with warm water (105° F.). The results obtained from this treatment are (1) the skins are washed free from dirt; (2) a considerable amount of calcium hydroxide is washed out, but the fixed calcium carbonate still adheres to the fibers and grain; (3) the removal of calcium hydroxide lowers the affinity of the fiber for water, and the pelts fall or decrease in thickness and increase in area, but under present local conditions do not fall to their normal condition, because the insoluble calcium carbonate to a certain extent fixes the skin in its swollen state, and should be decomposed with an acid giving a soluble salt. Unfortunately New South Wales basil-tanners do not use the right acids, for after the washing described above, the pelts are placed in a pickle containing sulphuric acid, and the calcium sulphate remains fixed,* affecting the quality of the finished leather.

The local pelts are not scudded, drenched, bated, or pulled down with organic acids or ammonium salts. They go straight from the hot water wash into the pickle, which contains sufficient sulphuric acid to neutralize all the lime, and leave them decidedly acid. The pelts worked under the above conditions do not return a first class sheep leather or basil. The process could be improved by removing surface lime with an acid giving a soluble calcium salt. Lactic, formic, or even hydrochloric acid could be used, by adding small quantities at a time, after the hot water wash, and using a paddle to keep the pelts in motion until they come down to the normal condition, when the small amount of lime left could be easily dealt with in the pickle.

Scudding has generally been looked upon as one of the most important parts of the process of preparing the pelts for the tan-liquors. Here, in New South Wales, it has been left out of the process, and, apparently, the tanners are satisfied with this

*See note, p. 309.

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change. Scudding is usually carried out by hand work, and the object in view is the removal of short hairs, grease, dirt, etc. If the pelt has been pulled down or neutralized, the scraping action of the scudding knife opens it out and removes the wrinkles. The class of pelts that we are describing contain no short hairs, and while a certain amount of grease could be removed from them, it is not probable that the results would pay for the extra labor on merino pelts. Cross-bred pelts may be improved by scudding, but after a fair amount of practical experience in dyeing basils that have never been scudded, we are inclined to think that hand-scudding could be left out of this process. At the same time, the skins require some mechanical action to stretch and remove wrinkles, and this work might be carried out by the aid of a machine or drum, after neutralizing. If these pelts were neutralized in a drum with hot water, and, say, lactic acid, they would be bigger and give better results at the setting-out machines. However, the improvements we suggest here are, (1), the removal of surface lime after washing with acids giving a soluble calcium salt; (2), some mechanical action to stretch and remove wrinkles from the pelts before they enter the tan-liquors.

The pickling process is carried out by placing the pelts in a solution containing common salt and strong acids, such as sulphuric, hydrochloric, and formic. Our local tanners use sulphuric acid, and keep the pelts in motion with the usual paddle wheel. The pickling solution described by Procter is made up with salt to a Barkometer density of 65° (sp. gr. 1.065), and the salt solution should then receive enough sulphuric acid to make 100 cc. of the pickling solution require 15 cc. of N/1 sodium hydroxide to reach the neutral point. The pelts, when they come out of this pickling solution, are placed in a saturated salt solution, and are then ready to be exported as pickled pelts, or they may be tanned in the local tanneries.

Procter's formula gives satisfactory results if the pelts are free from excess of lime, and he probably proved his formula by working on English pelts which one would expect to reach the pickle after, say, scudding and drenching, almost free from lime, or slightly acid. As a rule the pelts in New South Wales are decidedly alkaline before going into the pickle, and they also con-

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tain a large amount of calcium carbonate, as already described: therefore a considerable portion of the acid may be neutralized with the production of the insoluble calcium sulphate. Under these conditions it is not surprising to find the local pickling solutions much stronger than the one outlined by Procter. We can give particulars of pickling solutions used at one tannery as follows:—

TABLE SHOWING SODA REQUIRED TO NEUTRALIZE PICKLE.

| | Fresh pickle | | Used pickle | |
|---|---|---|---|---|
| No. | Density Barkometer | 100 cc. require cc. N/1 Soda | Density Barkometer | 100 cc require cc. N/1 Soda |
| 1 | 45 | 27.3 | 40 | 1.4 |
| 2 | 44 | 28.6 | 40 | 2.2 |
| 3 | 47 | 26.6 | 44 | 4.0 |
| 4 | 54 | 28.2 | 48 | 1.8 |
| 5 | 59 | 29.8 | 54 | 1.6 |

In the above example the acidity is high, but as the method of preparing the pelts does not remove the excess of lime, we may assume, with a few exceptions, that the acidity after neutralization is not a great deal stronger than Procter's pickle. Pelts to be exported sometimes go into a saturated solution of salt after leaving the pickle; but for tanning, they are simply thrown upon a tray to drain before removing to the tan-liquors.

Pickling, under normal conditions, sterilizes the pelts so far as putrefactive bacteria are concerned, and leaves them in a condition suitable for the export trade, or ready to enter the tan-liquors. It is not a hard and fast law that sheep pelts should be pickled before entering the tan-liquors if good leather results are to be obtained, but one advantage of it is that the pelts may be drained and left for several months when a boom is on in this particular industry, but the unpickled pelt would have to go at once to the tan-liquors to prevent decomposition. Procter states that pickled pelts do not consume as much tannin (sumac) as the unpickled. Another advantage of pickling is that the time required for tanning is much shorter.

The acid in the pickling solution is nearly all fixed by the pelt, and the outer solution retains only a small portion. The salt diffuses through the pelt and the outer solution shows no variation. Apparently no salt is fixed by the pelt, and the acid is

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generally supposed to be held by a weak chemical combination which is unstable unless there is weak acid in the outer solution. The pelt can be washed free from acid if it be suspended in running water.

The amount of acid used in pickling would destroy the pelts if no salt were used. The acid pelts have a great affinity for water, and when no salt is present they absorb water to such an extent that they are abnormally swollen, and the fibrous and cellular structure is partially destroyed, adversely affecting the quality of the resulting leather; so that pickled pelts, which retain a large amount of acid, should never be placed in water or tan-liquors that contain no salt, or the outer solution should contain a substance capable of exerting an osmotic pressure which successfully resists the osmotic pressure or affinity for water of the acid-proteins in the pelt, and abnormal swelling is then repressed.

The pickled pelts are tanned with tannin extracted from wattle bark of various kinds, and opinions vary as to which species gives the best color. Adelaide bark (*Acacia pycnantha*) is supposed to give a slight reddish color to the basils, and this is probably due to exposure, as this bark, when bagged, always shows more red than the New South Wales bark; so that we may say that Adelaide bark is more inclined to be affected by sunlight, or it is more exposed before reaching the tanneries than, say, the green wattle (*Acacia decurrens*) and its varieties. The bark to be leached is placed in large spenders and treated according to the theory of the man in charge of this work. Cold water is always used, and there is no system common to the majority of the tanneries, unless it be the one of using a salt solution for leaching. The tan-liquors all contain salt, and in the majority of cases these salt-liquors are pumped back on to the bark, and even the fresh bark at times receives salt water, so that the result is a large accumulation in both spenders (leaches) and tanyard liquors. Just what concentration of salt there is in the tan-liquors is beyond our knowledge, but we are probably right when we state that the majority contain sufficient to prevent the pickled pelts from swelling excessively in the first liquors. The apparently weak point in this system is the effect of the salt and faintly acid solution on the solubility of the tannins, and one would not expect to get the good results that are obtained when only water

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is used. The salt, by keeping out of solution the difficultly soluble red tannins, is probably the means of keeping the basils a good color, and if one were to leach bark with water under the press-leach system, a higher percentage of tannin might be extracted, but it is quite possible that the color of the basils would be adversely affected. However, this is another matter we hope to deal with in our research work.

Under local conditions the pelts are tanned with the aid of paddles. Each lot of pelts receives 4 to 8 liquors, and the paddles are running, in some cases, night and day. These pelts are thoroughly tanned in three days, using the paddles only in the working hours. The pelts go into a paddle box, and stay there until they are tanned, when they are thrown out to drain over-night, and then prepared for the setting-out machines. Sometimes sulphuric acid is added to the tan-liquors if the pelts show up a blue color (iron stain), but in the majority of cases an excess of acid is added in the pickle.

The bark consumed averages about 1 ton (Adelaide) for 150 to 160 dozen, costing about 1s. to 1s. 2d. per dozen basils. The basils or tanned sheep pelts are now drained, oiled, and set out. The setting-out machine stretches and lays the skin down flat. One operator can set out 900 basils per day, using a machine somewhat similar to the one described for fleshing, but differing in the set of knives. The skins are now dried, and pass through a staking machine, which stretches the dry basil, leaving it soft and pliable.

We have already dealt with several weak points and suggested improvements. Taking the average final products, we note that the ash (8 per cent.) is high, showing an excess of calcium sulphate and sodium sulphate and chloride. Leather exported to South Africa must not show more than 2 per cent. ash, and some New South Wales basils have been held up owing to their high percentage of ash. This trouble could be prevented by removing the lime from the pelts with an acid giving a soluble calcium salt, and the basils should also be thoroughly washed after they are tanned.

A number of finished basils after a few months show the effects of free sulphuric acid in the leather, becoming very red, with hard and brittle grain. This free sulphuric acid trouble can only be

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adjusted by controlling the pickling process, and no constant amount of acid will suit all tanneries. A hard water used for leaching bark would neutralize a large amount of acid and affect the concentration of the acid in the skin. Adding sulphuric acid to the tan-liquors is a bad practice.

We wish to thank those gentlemen who have assisted us to carry out the work of reviewing this important industry, and our thanks are especially due to the late Mr. McLaurin, and Messrs. J. Swinbourne, Jas. Swinbourne, Hale, and H. Whiddon, for permission to examine their various plants, and also Messrs. Bradley, Nugent, W. Gabb, Monk, and Hannah for the generous manner in which they have always placed their practical experience at our disposal.

When pointing out the several weak links in this industry we also desire to acknowledge the valuable work of the pioneers who placed fellmongering, wool-scouring, and basil-tanning on a solid foundation, and although we advocate improved methods scientifically controlled, we yet recognize the valuable pioneering work which makes improvements possible.

## Discussion.

Mr. A. B. Hector inquired whether anything was done in New South Wales in the extraction of wool fat?

Mr. Griffiths asked whether the authors had tried the use of lime-sulphur mixture in painting the skin, *i. e.*, the preparation obtained by boiling lime and sulphur together in water?

Mr. B. J. Smart said that in the plumping process, as practiced in England, he understood that for some leathers the use of lactic acid did not have the tendency to rot the leather so much as sulphuric acid.

Mr. A. M. Wright said that in New Zealand it was usual to wash the skins thoroughly in fresh water. Lime and sodium sulphide paint was used for something like 1½ million skins per annum, and this method was considered to give greater control than sweating. He thought that where results were eratic, this arose from underliming, from not adequately drenching the skins.

Dr. R. Greig-Smith said that skin substance was really a kind of gelatin, and that the action of lime seemed to be to loosen the fiber; but in the case of tripe, which is another kind of gelatine,

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its action is to harden the fiber. He would like to know the reason for the difference.

MR. COOMBS, in reply, said that the fat was not usually recovered from the wool, except when it became necessary to prevent the contamination of a clean stream of water. With regard to the use of lime-sulphur preparation, he said the results were too variable. As regards the choice of acid to be used in plumping, lactic was fairly expensive, while sulphuric was cheap and removed the iron stains more completely than lactic; and with regard to the action of lime on the skin substance, it at first made a very firm combination, and it was only after some days that the pelt became soft and pliable.

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## NOTE ON DELIMING WITH SULPHURIC ACID.

*By L. Balderston.*

The statement in the preceding paper (page 303) that lime is fixed in sheepskins by the use of sulphuric acid pickle is open to question. It is reasonable to suppose that when limed skins are treated with sulphuric acid the calcium sulphate formed in the skin would on account of its slight solubility remain there. Some experiments a few years ago on the use of sulphuric acid for plumping showed that heavy limed hides soaked 24 hours in 1 per cent. sulphuric acid were almost free from lime, and the lime removed from the hide was found in the solution. These facts led the writer to question the statement above mentioned in regard to sheepskins and to try the experiments here described.

A piece of dry sheep skiver about 8 by 10 inches in size was soaked up with water and then put for several days in milk of lime. It was then rinsed and dried at room temperature and cut in two. One part, weighing 6.75 grams was soaked for 2 hours and 40 minutes in a pickle containing 1 per cent. sulphuric acid and 6 per cent. salt, the total volume being 500 cc. It was then rinsed and soaked in 200 cc. of cold water half an hour. Both parts were now ashed. The ash of the pickled piece was 1.7 per cent. of its dry weight, including only 0.04 per cent. of lime. The other piece showed 8.2 per cent. ash, of which about half was lime. The lime recovered from the pickle in which the first piece

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was soaked amounted to more than 4 per cent. of the dry weight of the piece. It thus appears that 99 per cent. of the lime was removed from the skin in 2 hours and 40 minutes by a sulphuric acid and salt pickle.

The conditions of the experiment were not characteristic, because the amount of the pickle was much too large, being some seventy times the weight of the skin, instead of seven times, which would be nearer a practical ratio. It is probable that with such a ratio the proportion of lime removed would not be so great. The solubility of calcium sulphate in pure water is 1.8 parts per 1,000, being the same for hot or cold water. If the skins contained 4 per cent. lime, equivalent to about 9.7 per cent. of calcium sulphate, and the weight of pickle was ten times that of the dry skin, it is evident that the calcium sulphate could not all be dissolved in the pickle unless its solubility in the sulphuric acid and salt solution is greater than in pure water.

In order to test this point, a quantity of pure precipitated calcium sulphate was prepared from calcium chloride, being washed until the wash water was free from chlorine. The wet precipitate was then placed in 200 cc. of a solution containing 1 per cent. sulphuric acid and 6 per cent. salt and allowed to stand half an hour with frequent shaking. The solution was now filtered from the remaining calcium sulphate and the lime determined by precipitation as oxalate, and ignition to CaO. The percentage of lime was 0.26 per cent., corresponding to 0.63 per cent. of calcium sulphate, three and one-half times as much as pure water will dissolve.

The average ash of New South Wales sheepskin leathers is given on page 307 as 8 per cent. The authors do not state how much of this excessive ash is calcium sulphate, and since sodium sulphate and common salt, both highly soluble, are also present, it is not necessary to assume that any calcium sulphate contained in the leather is in any sense "fixed."

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## NITROGEN IN TANNING MATERIALS.*

*By Hugh Garner Bennett, M.Sc., F.C.S.*

As a side issue in certain other investigations, the author was in need of information as to the amount of nitrogeneous matters in the common tanning materials. Little information upon this point was obtainable from the usual books of reference, and in consequence, nitrogen determinations have been made with these materials.

The more commonly employed tanning materials were found to exhibit considerable differences in their nitrogen content, varying from one to about twelve parts nitrogen per thousand. It was also observed that the nitrogen content of a tanning material is characteristic of that material, in the same sense as the tannin content is characteristic, *i. e.*, the percentage of nitrogen in any material is not constant, but is approximately so within limits. Hence the nitrogen content supplies another criterion for the identification of a tanning material. The results in the following table are to some extent typical of the materials in question.

| Tanning material | cc. N/10 acid per 1 gm. material | % N | cc. N/10 acid per 1 gm. tan | mgms. N per 1 gm. tannin |
|---|---|---|---|---|
| Myrobalans..... | 4.0 | 0.56 | 12.9 | 18.1 |
| Valonia (cup)..... | 2.05 | 0.29 | 7.4 | 10.4 |
| " (beard)..... | 2.45 | 0.34 | 6.4 | 9.0 |
| Natal bark..... | 6.2 | 0.87 | 19.2 | 26.8 |
| Sumac..... | 6.2 | 0.87 | 25.1 | 35.2 |
| Lentisco..... | 8.4 | 1.18 | 49.4 | 69.2 |
| Quebracho wood..... | 1.2 | 0.17 | 6.0 | 8.4 |

It being improbable that all the nitrogen would be extracted from these materials in leaching, it was thought of interest to make nitrogen determinations of various extracts. The percentage of nitrogen in an extract is a figure of little interest or significance, being dependent upon the degree of concentration to which the extract has been subjected, *e. g.*, whether the extract be liquid or solid. If, however, results be calculated as nitrogen per unit tannin, they at once become significant and to a large extent characteristic of the extracts in question. The results may be usefully stated as "milligrams nitrogen per gram of tannin," which results may be called for convenience the "nitrogen value" of the extract.

* *Collegium*, London Edition, January, 1916, pp. 1–4.

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The nitrogen values of extracts—like the percentage nitrogen in dry materials—are approximately constant and characteristic of the particular materials. Quebracho extracts, for example, have nitrogen values ranging from 1.9 to 2.6, with an average of 2.3. By reference to the results with quebracho wood, it will be observed that about 27 per cent. of the nitrogen is leached out in extract manufacture. Myrobalans extract has an average nitrogen value of 8.2,—45 per cent. of the nitrogen of myrobalans being leached out.

It will be clear that in these nitrogen values we have also a criterion for determining the composition of mixed extracts. Blended extracts, for example, made from quebracho and myrobalans, will have a nitrogen value between 2.3 and 8.2, according to the proportions of the two ingredients.

If per cent. of myrobalans $= x$ and nitrogen value of mixed extract $= N$; then,

$$8.2x + 2.3\ (100 - x) = 100N$$

Hence, in the mixed extract of this description recorded in the following table:

$$8.2x + 2.3\ (100 - x) = 100 \times 4.3$$

$$\therefore\ x = 34 \text{ per cent.}$$

Of course this is an approximation only, as the nitrogen values of pure extracts vary to some extent. Still this mode of procedure is capable in some cases of yielding useful information.

Some typical results for various extracts are as follows:

| Extract | cc. N/10 acid per gm. material | % N | cc. N/10 acid per 1 gm. tan. | Mgms. N per 1 gm. tannin |
|---|---|---|---|---|
| Quebracho (solid) | 0.90 | 0.126 | 1.4 | 1.9 |
| " liquid 1. | 0.75 | 0.105 | 1.8 | 2.5 |
| " " 2. | 0.57 | 0.080 | 1.9 | 2.6 |
| " (bleach) 2 | 0.63 | 0.088 | 1.6 | 2.2 |
| " " 3 | 0.66 | 0.092 | 1.7 | 2.4 |
| " (mean :—) | — | — | — | 2.3 |
| Myrobalans 1. | 1.45 | 0.204 | 6.0 | 8.4 |
| " 3. | 1.44 | 0.202 | 5.55 | 7.8 |
| " (mean :—) | — | — | — | 8.2 |
| Mixed: Quebracho and myrobalans | 0.80 | 0.112 | 3.1 | 4.3 |
| " " " " | 0.78 | 0.109 | 2.7 | 3.8 |
| Chestnut | 0.56 | 0.079 | 2.1 | 3.0 |
| Hemlock | 1.26 | 0.177 | 4.5 | 6.3 |
| Cube gambier | 3.2 | 0.450 | 7.7 | 10.8 |
| Block " | 3.1 | 0.435 | 11.6 | 16.4 |

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It will be noticed that the nitrogen values of gambier are not only comparatively high, but also not very constant. This is doubtless due to the fact that gambier is an extract which contains a very variable amount of insoluble and unextracted matter; in short, gambier is an extract which is very badly manufactured. Nevertheless, the nitrogen value is even in this case of some value, for it is at any rate a check upon the addition of nitrogenous matters of animal origin, which are said sometimes to find their way into gambier.

It is quite possible that this determination of nitrogen values might yield another criterion for detecting the adulteration of extract with wood pulp. Not having any wood pulp extract to hand, the writer has been unable as yet to determine its nitrogen value, but its nature and origin make possible that its nitrogen content will be comparatively great. If wood pulp contains nitrogen in the same order of quantity as the dry tanning materials tested above, its presence in chestnut extract should be easily demonstrated by a determination of the nitrogen value of the suspected extract.

The nitrogen values of the dry materials may be calculated in the same way as for extracts, but do not possess quite the same value, being less constant for any particular material on account of their dependence upon two variables. Moreover, mixtures of dry materials are not often met with. In the case of sumac and lentisco, it is interesting to note that a nitrogen determination would be at any rate a confirmatory test for the adulteration of the former with the latter. In this case the tannin percentage is reduced whilst the nitrogen content is raised. Hence, if *both* these features are noticed, there is evidence of such admixture.

It is probable that the percentage of nitrogen leached out under tannery conditions will differ from that extracted in the manufacture of extracts, but some of this nitrogen is certainly leached out, and it is necessary to point out that in estimating nitrogen in tan liquors, the nitrogen originating in this way should be carefully distinguished from the nitrogen obtained from the goods.

All the nitrogens here recorded were by Kjeldahl's method. The digestion is slow, and it is not wise to employ permanganate

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as accelerator so long as the acid is turbid. When a clear red-brown is obtained, however, the digestion is soon completed if the useful suggestions of Mr. A. T. Hough (*Collegium*, 1915, p. 126) be adopted.

## BOOK NOTICE.

THE SHOE INDUSTRY, by Frederick J. Allen, A. M., Investigator of Occupations for the Vocation Bureau of Boston. Published by the Vocation Bureau of Boston, 6 Beacon St. Price $1.25; 327 pages, 5¼ by 8 inches; 22 illustrations.

An idea of the contents of this book may be obtained from the chapter headings: Historical Sketch; Shoe Machinery; Last-making; Pattern-making; Leather; The Department of Shoe Manufacture; Methods in Shoe Manufacture; The Upper Leather Department; The Stitching Department; The Sole Leather Department; The Making Department; Finishing, Treeing, Packing and Shipping; Employment Conditions and Supplementary Material; An Explanation of the Terms Used in Shoemaking.

The book is written in clear concise style, and gives full and authoritative information on all the methods and processes used in the manufacture of shoes. Many statistics are also given. The illustrations include diagrams showing the construction of the different types of shoe, and pictures of a welt shoe at each stage of making. There is a bibliography of 34 titles on shoe manufacture, and a list of American shoe and leather journals.

## ABSTRACTS.

**Brazilian Tanning and Dyeing Materials.** CONSUL GENERAL ALFRED L. MOREAU GOTTSCHALK, Rio de Janeiro, in *Commerce Reports*. On February 4, 1916, this office reported, in reply to an inquiry from the Department, that there appeared to be no likelihood of any notable exports from Brazil of mangrove bark. This results from certain laws which do not permit deforestation of the foreshores. It was stated that without a special concession from the Brazilian Government and a suspension of these laws nothing could be done. A movement initiated in the local press on the subject of mangrove bark has, however, led to proposals from a number of persons who have offered samples and made proposals to furnish various vegetable tanning as well as dyeing materials. These

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referred largely to the bark of the barbatimao. The most abundant source of tannin in the country is the mangrove. Its bark contains 36 per cent. and the leaves 24 per cent. of tannin. Next in importance come angico, which is encountered all over the Republic, and the barbatimao tree. The former contains about 40 per cent. of tannin; the bark of the latter reaches sometimes 48 per cent. Barbatimao abounds in the State of Minas Geraes, is present in large quantities in Sao Paulo and Goyaz, and is found generally in the temperate portions of Brazil. There is a slight local trade in it, the bark, roughly cut, being sold in small bundles. It is known to the smaller native industry of Brazil as a powerful styptic and is used extensively in household industry as a red dyestuff. Its botanical name is *Stryphnodendron barbatimao,* Mart. The angico (*Piptadenia rigida,* Benth.) is a leguminous plant found in abundance throughout the Republic. It is much used locally in tanning the finer sort of skins. The Monjolo branco de Espinho (*Enterolobium monjolo,* Mart.) exists in great abundance in the States of Rio de Janeiro, Espirito Santo, and Minas Geraes. In the city of Campos it is extensively used as a tanning material. Its price is said to be about 19 cents per arroba of 32.38 pounds. The Burahem de Casca doce (*Glycisophyllum Burahem,* Mart.) is a powerful astringent, whose dry extract is said to have been successfully employed in Europe for medicinal purposes. It offers an excellent tanning material. Of the family of the myrtaceaes, the jiquitiba rose (*Couratari legalis,* Mart.) is a very large, thick-barked tree, growing, it is said, to a height of nearly 100 feet and attaining a trunk diameter of 16 to 23 feet. Its fibers are excellent for rope making and furnish a material for manufacturing paper. They contain, like the bark, a useful astringent and tanning material. It is present in most of the States of the Brazilian Republic. Besides these there are the Sapucaia (*Lecythis pisonis,* Cambes.), the Araca pellada (*Psidium araca,* Mart.), Matta pao (*Urostigma hirsuta,* Miq.), Vinhatico do Campo (*Pythecolobium gummifera*), Grauna (*Melanoxylon brauna*), Bacorubu (*Schyzolobium excelsum*), and other plants described by naturalists as containing various percentages of tannin and popularly known and used by the natives in the cottage tanning industries.

Brazil, according to its botanists, is capable of furnishing a profusion of materials for purely dyeing purposes seldom met with in one single country. The list ranges from black to faint yellows and rose. Information regarding a number of these, as compiled by numerous Brazilian authorities on the subject or published in various exposition catalogues, etc., has been summarized by this consulate. It is particularly interesting to consider Latin American tropical sources of supply, particularly at this time, when the European war conditions have closed to the world's markets the customary sources of supply of aniline dyes. Cheapness, perhaps, rather than the degree of solidity or of fastness, has favored the widespread use of these colors, chiefly of German origin. There are in Brazil to-day not a few persons who are speculating upon the possibilities of the world's returning, for a time at least, to the use of some of the old-

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time vegetable dyes, known to former generations, which within comparatively recent years have been supplanted by the vastly inferior, though cheaper, artificial aniline colors. Of these old-time vegetable dyes, Brazil possesses an almost endless variety. The very name of the Republic is derived from the term originally given to the most famous product of its early colonial days, the "pao Brazil," a wood, the color of brasas, which was braza (fiery red)—the "Brazil wood" of commerce, familiar to older American importers.

Indigo (*Indigofera anil,* Linn.), locally known as anil, grows spontaneously throughout Brazil and is found in great profusion in Amazonas, Pernambuco, Espirito Santo, Minas Geraes, and Rio de Janeiro. It was cultivated extensively during the Colonial period, when thousands of tons found their way to Europe. To-day its cultivation has been practically abandoned, as the foreign demand has ceased. The plant still grows wild in the sections of the country mentioned. It came originally from India, local historians state. With that care which certain Colonial governors used in propagating species from one Portuguese colony to another, it was domiciled and found to thrive luxuriously in Brazil. Its introduction is due to the Marquis of Lavradio, who in 1770 cultivated it in the State of Rio de Janeiro. It passed rapidly to Pernambuco, which at one time had, at the village of Bebribe, a factory for the extraction of the dye. In 1783 it was made the subject of Government ordinances tending to foster its export. It continued, until the end of the 18th century, to be an important item in the country's exports. Pao cravo (*Dycipelltum caryophillotum,* Pees.) yields an intense black die. It is used extensively throughout the interior of Brazil, in households, for dyeing cotton cloth. Found in all the States of the Republic, it is most prevalent, apparently, in Espirito Santo. Brauno, or Maria preta, or Grauna (*Melanoxylon brauna,* Schott.), is a bark producing a deep black dye. The sap also furnishes a dark-hued coloring material used in certain interior sections with success as a hair dye. It is found in Minas Geraes, Espirito Santo, and Bahia. Arariba (*Pinckncia rubescens,* F. Allem.), yields both a yellow dye and a blood-red dye, used in cottage industry for coloring nets, hammocks, baskets, etc. It occurs in Espirito Santo, Rio de Janeiro, Minas Geraes, and Bahia. Urucu (*Bixa orellana,* Linn.) has seeds which yield a coloring matter, known as annatto. It furnishes a variety of yellow tints. It is extensively employed in coloring butter, cheese, confectionery, and other articles of food. It grows in great profusion throughout the tropical States of northern Brazil and in the West Indies. The juices of fructos de pacova (*Renealmia exaltata,* Rosc.) furnish a red dye of exceptional fastness, employed often as a writing ink. It is found throughout Brazil in varying quantities. Pao sangus (*Vismia latifolia,* Choisy) is present apparently in all the States of the Republic. The coloring principle is of a blood-red tint.

The following are also plentiful in Brazil: Anil assu (*Eupatorium tinctorium,* Pohl.). This yields a blue-black dye very similar to that of real indigo. It is said to be easier to extract the dye from this variety

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than from the real indigo. The plant itself is very abundant. Anil trepador, or climbing indigo (*Cissus tinctoria,* Mart.), a member of the Ampellidaceæ family. Both branches and fruit of this plant produce a rich blue dye, much used by the Indians. Another Anil trepador (*Cissus sicycides,* Linn.) likewise produces a blue dye. Brincos de Princeza (*Fuchsia integrifolia,* Camb.). Found in Minas Geraes, Bahia, and Rio de Janeiro, as well as Esperito Santo. It yields a black dye. Camarambaia (*Jussioea scabra,* Will.). Occurs in Bahia, Minas Geraes, Rio de Janeiro, and Rio Grande do Sul. It furnishes a dye of inky blackness. Candua (*Gladonia sanguinea,* Mart.). A lichen found very generally throughout the State of Minas Geraes. It furnishes, as its botanical name indicates, a blood-red dye. Caparosa (*Ludwigia caparosa,* Baill.). Seen in Minas Geraes, Bahia, and Goyaz; supplies a yellow dye. Carajuru, or Carajiru (*Bignonia chica,* Humb). A creeper abounding in the Amazoniana regions of Brazil. It is a favorite source of coloring matter among the Indians, who for generations have extracted dyes from the juices of the plant. A decoction of the leaves deposits, after boiling, a fine red powder which is regularly sold in the native markets. Catigua (*Trichilia catigua,* St. Hil) abounds in Minas Geraes and portions of southern Brazil. It furnishes a light reddish dye. Cruz de Malta (*Jussioea pilosa,* H. B. K.). Yields a yellow dye. Fuchsia (*Fuchsia montana,* Camb.). Abounds principally in Minas Geraes. It yields a black dye. Gravata de tingir (*Aechmea tinctoria,* Mez.). One of the Bromeliaceæ, present in quantities in the States of Rio de Janeiro, Espirito Santo, Minas Geraes, Alagoas, and Ceara. The fiber of the plant, as well as the yellow dye obtained from the root, are extensively used by the Indians. Macucu, or Maca de fogo (*Licania glabra,* Mart.). One of the Rosaceæ, is found principally in the States of Para and Amazonas. A black dye is extracted from the resinous substance contained in its small egg-shaped fruit. Another tree of the same family (*Couepia chrysocaliz,* Benth.), also abundant in the country, produces a similar black dye. Negreira (*Jussioea larnoteana,* Camb.) yields a black dye. Roxinho, pao roxo, or guarubu (*Peltogyne Guarubu,* Frei Allem.) is found in Espirito Santo, Minas Geraes, Bahia, and Rio de Janeiro. Both bark and wood yield coloring matter of a reddish tint. Sangue de drago or "dragon's blood" (*Croton salutaris,* Casar.), of the Euphorbiaeceae family, yields a red dye. Tatagiba do brejo (*Maclura braziliensis,* Endl.) is abundant in the south of the State of Bahia, in Rio de Janeiro, and Espirito Santo. It yields a yellow dye. Tatagiba do espinho (*Maclura affinis,* Miq.), abundant throughout Brazil, is known under various local names—in Sergipe as Amoreira, in Pernambuco as Espinheiro branco, and as tataoba, tai-tai-y, tatarema, jataiba, fustete, etc. It also yields a yellow dye. Tatauba or tatagiba (*Morus tinctoria,* Mill.), of the artocarpus family, is well known in Minas Geraes, Goyaz, and Rio de Janeiro. It contains a yellow dye. Urucurana (*Croton Urucurana,* Baill.) and also the *Croton Erythryna,* Muell., furnish red dyes. While all the plants mentioned are found over a great part of the vast area of the Brazilian Republic, little or no tech-

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nical use seems to be made of the coloring matters present in them beyond the fitful demands of the household industry as mentioned. In order to procure these wares it would be necessary to have a representative here who would interest the small farmer or the rural communities in collecting for him the small lots that eventually would form a shipment of suitable size. The superiority of some of our foreign competitors in Brazil (notably the Germans) has been that their commission merchants, located on the spot at Rio de Janeiro, have always attended to such orders from their merchants at home.

**Algarrobilla Supply Available in Chile.** *Commerce Reports.* Samples of algarrobilla, which has a recognized value as a tanning material, and is also available as a mordant in dyeing, have been received from Chile through the Seattle branch office of the Bureau of Foreign and Domestic Commerce. They were forwarded by Commercial Agent W. B. Henderson, who received them from the consular representative of a South American country. The present year's crop has been on the market since March 15, and the material may be obtained in large quantities by manufacturers in the United States. It is stated that the price is about $5 per 100 pounds. Communications may be addressed either to a firm of exporters in Chile or to the consular representative mentioned, who spent a number of years as traveling agent for a Pacific Coast firm in Chile, but is now located at Seattle. These addresses may be obtained from the Bureau of Foreign and Domestic Commerce or its district offices. The samples may also be inspected at these offices. Refer to file No. 116.

**Supply of Brazilian Mangrove Bark Offered.** CONSUL GENERAL ALFRED L. GOTTSCHALK, Rio de Janeiro, in *Commerce Reports.* A citizen of Sao Paulo has written the Rio de Janeiro consulate general that he is in a position to export mangrove bark to the United States. He states that the bark must be dried before it can be shipped, and that this bark loses 50 per cent. of its volume during the process of drying, necessarily increasing the selling price. He is forced to buy the bark when wet, and then to sell it after it has been dried and decreased in volume. This bark is shipped in jute sacks so as to prevent injury to the material, and these sacks cost about $0.25 each in American currency. The additional cost must be met by the buyer. The selling price of this bark (locally known as casca de mangue) is about $115, American currency, per ton of 2,204.6 pounds, Paranagua, State of Parana, loading, freight, and bagging to be paid by the buyer. Payment is to be made against documents, Paranagua. Large shipments of this bark cannot well be expected on account of certain local legislation preventing the cutting of mangrove bark along a defined coastal region.

**New Method for Removing Hair from Hides.** CONSUL HOMER W. BYINGTON, Leeds, England, in *Commerce Reports.* Since the war sodium and arsenic sulphides, which are largely used in the unhairing of hides, have reached almost prohibitive prices, and Mr. J. E. Pickles, of the

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leather department of the University of Leeds, recently read a paper entitled "The Depilation of Hides and Skins," before the Yorkshire Section of the Society of Chemical Industry. The paper described how experiments at the university have shown that a substitute is to be found by boiling lime with sulphur, and then adding soda in the calculated amounts to give the same effects as sodium sulphide. The sulphur was added to the lime without slaking, and, if necessary, boiled with the lime until all the sulphur was dissolved. This gave a yellow-colored liquid. The soda could be added during or after slaking. This lime had been used in the experimental tannery of the university, and two packs of calfskins for chrome tanning were ready for unhairing in four days, and as far as could be seen there was no difference between these skins and those unhaired with sodium sulphide. In the case of a pack of hides for chrome sole leather, more soda was added to the lime in order to increase the swelling, and these hides also were unhaired in four days. It had also been used for skins intended for vegetable tanned dressing leathers with equally good results.

**Oxygen Demand of Sewages.** F. W. BRUCKMILLER, *Jour. Ind. and Eng. Chem.*, May, 1916, pp. 403-4. The dilution method employs aerated distilled water with which various dilutions of the sewage are made and incubated for 10 days. This method was rejected because it has large opportunity for error, and consumes much time. It is not adapted for field work because it requires too much apparatus. The method of Lederer was found satisfactory. Varying quantities of $NaNO_3$ are added to a constant quantity of sewage. The sample which on incubation remains sweet and free from sediment is regarded as having received the proper amount of oxygen. Residual nitrates and nitrites may be determined at leisure if the samples are chloroformed after incubation.

**Ceanothus Velutinus (Snow Bush) as a Source of Wax and Tannin,** C. C. SCALIONE and H. S. BLAKEMORE. *Jour. Ind. and Eng. Chem.*, May, 1916, pp. 411-13. This plant is a branching bush, from 2 to 6 feet high, with broad leaves about 3 inches long having resinous smooth upper surfaces. It grows in an area extending from Colorado to the Coast Range and from San Francisco to the Columbia River. Petroleum ether extracted 7.3 per cent. of a brittle wax from the leaves, which was examined in considerable detail. The leaves contain 17 per cent. of a catechol tannin. Tanning tests showed good results as to color and quality of resulting leather. The supply available in the Shasta National Forest and elsewhere is large.

**Tannin-containing Barks and Woods for the Leather Industry.** J. PAESSLER. *Holzmarkt*, through *Ledertechnische Rundschau*, Jan. 20 and 27, 1916. Review of materials available in Germany and Austria-Hungary. Oak forests used for bark cover more than 400,000 hectares in Germany (about 1,000,000 acres). Young trees, from 12 to 25 years old, are cut in the spring. The bark, called Spiegelrinde or Glanzrinde (smooth bark)

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is dried before being sold. The wood is sold as fuel. The proper age at which to cut the young oaks for bark is when the bark at the butt begins to form "ross." At this age the tannin content is highest, from 6 to 16 per cent., averaging about 10 per cent. Scarcity of tanning materials now causes the bark of the smaller branches to be peeled, in spite of its poverty in tannin. Herr Gutschow has devised a process by which trees cut for timber at other seasons than spring may be peeled, by the use of steam. The bark of older trees is not useless for tanning, but ross, which is from 10 to 40 per cent. of the whole, has little tannin. It is proposed to place this on the market with the ross removed.

Fir bark (fichtenrinde) is a by-product of the lumber industry. Large quantites of it have been imported into Germany for years, while other quantities were wasted. The bark of trees cut in early winter cannot be peeled, but that of trees cut in February, if the logs lie until spring, may then be peeled. The damper the climate and the warmer the winter, the more easily can the bark of trees that have thus lain until spring be peeled. Winter is the best time to cut the trees for timber, not only because more labor is available then, but because lumber made from winter-felled trees lasts better. The logs cut in spring or early summer are apt to crack in drying after they have been peeled. The bark may be chipped from winter-felled trees, but such bark is mixed with a considerable amount of wood, which contains no tannin. The peeled bark is piled on heaped-up twigs and trimmings to keep it off the ground while drying. The pieces are about 3 feet long, and are stacked flesh side down. The Gutschow process may also be used for fir bark, and it is to be hoped that it will result in saving much of that which has heretofore been wasted because of the impossibility of peeling it. Fir wood is valueless as a source of tannin. The cones and needles contain tannin, but not enough to pay for extraction. The same is true of the needles and twigs and small branches which make up the refuse from lumbering. In general, the tannin content of fir bark increases with the age of the tree. The ross of the bark contains only from 2 to 4 per cent. of tannin, so the best bark is that having thick flesh and thin ross. Very old bark may be rossed to good advantage, but not that of middle weight and age. Not only age, but locality influences the quality of fir bark. That which grows on thin poor soil has thin flesh and is low in tannin content. On rich soils in well-watered regions, the growth of the trees is more rapid, and the formation of ross begins at a later age, the flesh being relatively thicker. Under these conditions a tree may reach the age of 80 years with an almost smooth bark. This type of bark is the best. The tannin content of fir bark varies from 7 to 18 per cent., averaging about 11.5 per cent.

Other barks which are of value as tanning materials are willow, birch, larch and walnut. All these must be dried as promptly as possible and kept dry. Willow bark is a particularly valuable material, and none of it should be allowed to go to waste. Two species are found in the German markets, the tannin content being from 8 to 14 per cent., averaging about 10 per cent. Birch and larch barks are somewhat similar in

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behavior as tanning materials, the latter being rather higher in tannin. Walnut bark is not much used on account of its low tannin content, from 5 to 9 per cent., but is now finding use on account of the scarcity of better materials.

Oak wood extract has been made extensively in Slavonia and southern France, largely from sawdust and refuse of oak lumber. Not much of this extract is available in Germany at present. The wood of young trees, such as are cut in Germany for bark, contains little tannin. Chestnut wood rises in tannin content with age, but the trees of 12 to 18 years, in contrast to oak, have a good percentage, and are extensively used for extract making. Heart-wood, sap-wood and bark all have tannin, so the whole may be ground together. Fresh chestnut wood, with a water content of from 35 to 45 per cent. contains from 4 to 11 per cent. of tannin.

L. B.

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## PATENTS.

**Discharging Sewage Tanks. British Patent 24,630.** W. JONES, Stourbridge, Staffordshire. A continuous method of discharging tanks employed in the "activated sludge" process of sewage treatment.

**Pneumatic Bed for Leather-working Machines. U. S. Patent 1,179,649.** OSCAR RIERSON, Peabody, Mass.

**Drying and Stretching Frame for Leather, Hides and Skins. U. S. Patent 1,180,023.** PETER J. DUNN, Irvington, N. J.

**Tanning Apparatus. U. S. Patent 1,176,633.** EDWARD WILSON, Bootle, Liverpool, England. The hides are attached to movable slats attached to a rotating frame, and as the frame rotates, the hides are dragged over fixed bars, and through the liquor.

**Bating Material. British Patent 22,753.** W. P. THOMPSON. Liverpool. Hides are bated by means of a material obtained by the decomposition of animal organs by the enzymes contained therein or by peptolytic enzymes; pancreatic gland, liver, gall, bowel, etc., are suitable starting materials; other albuminous bodies such as meat, glue, casein, etc., may be added; when decomposition is complete, the mass is heated to destroy the enzymes, and the liquid portion of the product is separated; it may be used as such or absorbed in kieselguhr, sawdust, etc.

**Artificial Leather. British Patent 100,038.** N. G. SCHEUER, Copenhagen. Artificial leather is made by impregnating linen duck with linseed oil or a varnish to which a little siccatur and Vienna red have been added, drying and sticking sheets of this material together with a mixture of 4 kilos heated wood-tar pitch, 2 kilos india rubber dissolved in benzene or the like, 4 kilos Vienna red mixed to thick consistency with French turpentine, and 2 kilos of powdered cork. The compound sheet is finally passed through pressure rollers.

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**Leather Cleaning Machine. U. S. Patent 1,180,306.** EDGAR W. MCQUAY, Ontario, Canada.

**Leather Stretching Device. British Patent 24,163.** G. ANGUS and R. S. HOWARD, Newcastle on Tyne.

**Tanning Agent. British Patent 24,196.** J. C. BYROM, Heaton Chapel, near Stockport. Waste sulphite extracts from the maanufacture of wood pulp by the sulphite process are converted into tanning agents by treating with hydroxy compounds of the aromatic hydrocarbons, carbolic acid, cresylic acids, and certain coal-tar distillation products (middle oil, heavy oil, and creosote oil), or with the amido compounds, or with naphthalene-disulphonic acid, or with mixtures of the same. Concentrated sulphuric acid may be added to the concentrated sulphite extract containing the hydrocarbons, for sulphonating.

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Journal of the

# American Leather Chemists Association

Vol. XI JULY, 1916 No. 7

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

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## The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, W. K. ALSOP, L. E. LEVI, } Past Presidents

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F. P. VEITCH, Leather and Paper Laboratory, Bureau of Chemistry, Washington, D. C.

## ELECTIONS.

### ACTIVE

C. M. Hulings, Cattaraugus Tanning Co., Olean, N. Y.
Alan Llewellyn Chapple, Rosendale, Torrington, Devon, England.

### ASSOCIATE.

C. N. Hammond, Muskegon, Mich.
Frank J. Norris, Keystone Leather Co., Camden, N. J.
Edward K. Smith, % Fred Rueping Leather Co., Fond du Lac, Wis.
Louis I. Simons, 164 Union St., Everett, Mass.

## CHANGES OF ADDRESS.

H. T. Wilson, to 901 Michigan St., Petoskey, Mich.
R. E. Porter, to Ashland Leather Co., Ashland, Ky.
Cudworth Beye, to 146 Summer St., Boston, Mass.

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## ADDITION TO BY-LAWS.

The following addition to the By-Laws has been adopted by a vote of 59 to 6, and will constitute section 15B:

All committee work under consideration and that which is to be presented at an annual meeting shall be in the hands of the Editor of the JOURNAL sufficiently early for him to have it printed in the JOURNAL issued at least one month previous to the annual meeting and copies shall be presented to members at the annual meeting.

## ADDITION TO METHODS.

The following addition to the methods has been adopted by a vote of 62 to 1: Add to paragraph 10 of the official method of tannin analysis the words "or Munktell's No. 1 F.," so that the paragraph shall read, "S. & S. No. 590, or Munktell's No. 1 F., 15 cm. single, pleated, filter paper shall be used for the filtration."

## THIRTEENTH ANNUAL MEETING.

Shortly before 11 o'clock on Thursday morning, June 1, 1916, the thirteenth annual meeting of the American Leather Chemists Association was called to order by President Louis E. Levi in the west salarium of the Marlborough-Blenheim at Atlantic City. The President's address appears elsewhere in this number.

The Treasurer's report is as follows:

GENERAL ACCOUNT.

| | | |
|---|---|---|
| *Receipts.* | | |
| Cash on hand May 1, 1915 | | $1,174.72 |
| Dues | $1,320.42 | |
| Interest | 9.50 | 1,329.92 |
| | | $2,504.64 |
| *Disbursements.* | | |
| Annual Meeting expenses | $152.50 | |
| Council Meeting expenses | 69.45 | |
| Secretary's expenses | 208.30 | |
| Committee expenses | 13.11 | |
| Printing, postage, envelopes, expressage, supplies, Sun policy, etc. | 219.14 | |
| From Journal Account | 198.28 | 860.78 |
| Balance on hand May 1, 1916 | | $1,643.86 |

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JOURNAL ACCOUNT.

*Receipts.*

| | | |
|---|---|---|
| From advertisers | $1,234.97 | |
| From back numbers | 23.25 | |
| From bound volumes | 242.30 | |
| From subscriptions | 102.45 | $1,602.97 |

*Disbursements.*

| | | |
|---|---|---|
| Journals (April, 1915, to May, 1916) | $1,282.38 | |
| Reprints | 132.38 | |
| Abstracts and translations | 49.45 | |
| Index | 43.09 | |
| Copyrighting Journal | 12.00 | |
| Bound volumes | 60.63 | |
| Editor's expenses | 220.87 | $1,806.25 |
| To General Account | | $ 198.28 |

SUMMARY.

| | | |
|---|---|---|
| Cash on hand May 1, 1915 | | $1,174.72 |
| Receipts, General Account | $1,329.92 | |
| Receipts, Journal Account | 1,602.97 | 2,932.89 |
| | | $4,107.61 |
| Disbursements, General Account | $ 662.50 | |
| Disbursements, Journal Account | 1,801.25 | 2,463.75 |
| Cash on hand May 1, 1916 | | $1,643.86 |
| Due from advertisers, bound volumes and dues | | $1,171.30 |

The Secretary's report showed a total of 163 active members on May 1 as against 160 a year ago. There have been 12 elections during the year, 9 resignations and 3 deaths. The number of associate members was 164, as against 152 a year ago, 8 having resigned and 2 died, while 22 new members were elected.

C. R. Oberfell and R. H. Wisdom were appointed a committee to audit the Treasurer's account.

The next item was the report of the Committee on Miscellaneous Methods, by L. Balderston, Chairman. This report appeared in the JOURNAL for March, 1916.

J. V. R. Evans, Chairman of the Committee on Methods in connection with Beam-House Procedure, read his report, published in the JOURNAL for May, 1916. In answer to a question Mr. Evans said he had not compared the method for free am-

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monia given in his report with that given by H. G. Bennett (this JOURNAL, March, 1916, page 103).

## SECOND SESSION.

No session was held on Thursday afternoon. The second session convened about 10.15 on Friday morning, June 2. At the request of the President, R. W. Griffith took the chair.

E. J. Haley presented a report from the Committee on Uniform Blanks for Tannin Analysis. The committee had procured from the commercial laboratories represented in the Association six forms of report. These were sent to all active members with the request that they indicate their preference. The six forms are as follows:

### No. 1.
### CERTIFICATE OF ANALYSIS.

SAMPLE: .....
MARKS: .....
FROM: .....
RECEIVED: .....
Specific Gravity .....
Degrees Twaddell .....
Moisture .....
Total Solids .....
Soluble Solids .....
Reds .....
Non-Tannins .....
Tannin .....
PURITY .....

**Analyzed According to the Official Method of the A. L. C. A. Rapid Slow Cooling Method.**

### No. 2
### ANALYSIS OF EXTRACT.
**According to the Official Method of the A. L. C. A.**

To .....
.....
Date Received .....
.....

| | | | | |
|---|---|---|---|---|
| Moisture ..... | | | | |
| Non-Tannins ..... | Total Soluble Solids | ..... | | |
| Tannins ..... | | ..... | | |
| Insolubles, Reds ..... | | | | |

Specific gravity .....
Weight per Gallon .....
Degrees, Twaddell .....
Remarks

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No. 3.

Received .....
Sample .....
From .....
Marks .....

| | |
|---|---|
| Gravity | Moisture |
| Twaddell | Tannins |
| Total Solids | Non-Tannins |
| Soluble Solids | Insolubles |
| Ash | Total |

Analyzed by the Official Method of the A. L. C. A.

No. 4.

Analysis .....
From .....
Mark .....
Received ..... Labor. No.....

| | |
|---|---|
| Specific Gravity | Water |
| Twaddell | Insoluble |
| Barkometer | Non-Tannin |
| Total Solids | Tannin |
| Soluble Solids | Total |
| Ash | |
| Acid | |

Analyzed by Official Method of A. L. C. A.

No. 5.

Laboratory No.
Material
Received
From
Marks

ANALYSIS

| | |
|---|---|
| Tannin | Total Solids |
| Non-Tannins | Soluble Solids |
| Insolubles | Ash |
| Water | Specific Gravity |
| Total | Twaddell |

Analyzed by the Official Method of the A. L. C. A. Slowly / Rapidly } Cooled

Comment

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No. 6.

Material .....
From .....
Marks .....
Date Received .....
Date Reported .....
Laboratory No. .....

ANALYSIS

Degrees Twaddell .....
Moisture .....
Total Solids .....
Soluble Solids .....
Insolubles .....
Non-Tannins .....
Tannin in Sample as Received .....

This Analysis was made by the Official Method of the American Leather Chemists Association

Fifty-nine votes were cast, 29 for No. 5, 12 for No. 1, 8 for No. 6, 3 for No. 3, and 2 each for Nos. 2 and 4. Three votes were void, because they made changes in the forms voted for.

W. H. Dickerson remarked that if a sample is sent to a chemist labelled hemlock extract, he will report on it as hemlock extract, stating the percentages of tannin, etc. The sample may not be hemlock extract at all, but the report seems to certify that it is. He advocated a form which would state that the analysis refers to tannin content, and involves no determination of the source of the material or the kind of tannin.

E. J. Haley mentioned a case in point. He bought some hemlock extract, the seller submitting the analysis of a reputable laboratory stating that the material was hemlock extract. The extract was resold to a tanner, who, detecting an unfamiliar odor, sent a sample to the same laboratory which had made the original analysis, asking whether it was pure hemlock extract. The answer was that it contained from 15 to 20 per cent. of foreign material. In the first case the chemist's report that it was hemlock extract had no other basis than the label on the bottle. In the second case there was no label, and he gave a report based on an actual examination.

On motion of Mr. Haley, the Association voted that it is de-

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sirable that a uniform blank for reporting tannin analyses be adopted.

C. R. Oberfell, Chairman, now read his committee report on the cure and disinfection of hides, which appears elsewhere in this number. A long discussion followed, the substance of which is given in the pages following the report.

### THIRD SESSION.

Friday afternoon, June 2: C. R. Oberfell in the chair.

Lloyd Balderston read a paper on the "Wear Resistance of Sole Leathers," describing some experiments with a piece of apparatus operating on small samples of leather. A long discussion followed. J. S. Rogers of the Bureau of Chemistry described laboratory experiments along the same line, and Dr. Allen Rogers, of Tanners' Institute, described an experiment comparing chrome and oak sole, where the tests were made by soling one shoe with one kind of leather and the other shoe with the other kind. Both the paper and the discussion will appear in the JOURNAL later.

Some further remarks on disinfection of hides followed, J. Y. Yocum calling attention to the advantage of using salt in connection with bichloride of mercury.

The Vice-president, E. J. Haley then took the chair, and C. R. Oberfell read the report of the Committee on Sulphonated Oils, printed in the May JOURNAL. A paper entitled, "Notes on Sulphonated Oil Analysis," by W. K. Alsop and L. A Cuthbert was next read by Mr. Alsop. This paper and the long discussion which followed are printed in this number.

### FOURTH SESSION.

Saturday morning, June 3, President Levi in the chair.

The auditing committee reported that the Treasurer's accounts were correct.

F. H. Small read a paper by Byron E. Parks on "The Fuel Value of Spent Hemlock Bark," which is published in this number.

J. S. Rogers, in offering his paper on the denaturing of egg yolk, said that the Government had been compelled to adopt this method because eggs intended for use in finishing alum-tanned leather might otherwise be used by bakers. Eggs condemned

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as unfit for food are separated, and the yolks barrelled, with the addition of 20 per cent. salt and shipped as tanners' eggs. Such material entering interstate commerce must now be denatured. Mr. Rogers' paper will be printed in a future issue of the JOURNAL, together with an abstract of the brief discussion which followed.

The Association then proceeded to the election of officers. Allen Rogers and H. H. Hurt were appointed tellers, to count both the ballots for officers and the vote on an addition to the By-Laws and an addition to the official method of tannin analysis.

The officers chosen were:

President—Charles R. Oberfell.

Vice-President—Charles Eachus.

Secretary-Treasurer—H. C. Reed.

Ordinary members of Council—W. K. Alsop, F. P. Veitch.

The vote on the amendment to the By-Laws was 59 for and 6 against. This addition to the By-Laws, which appears on page 324, will be section 15 B.

The proposed addition to the methods, permitting the use of Munktell's 1 F filter paper in the filtration of soluble solids, was adopted by a vote of 62 to 1.

The retiring President congratulated the newly-elected officers.

On motion of Mr. Eachus, a vote of thanks was extended to the retiring President.

Final adjournment was reached about noon.

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## COUNCIL MEETING.

Immediately after the adjournment of the annual meeting, the new Council met, Messrs. Oberfell, Eachus, Reed, Small and Alsop being present.

It was decided not to change the representation of the A. L. C. A. on the joint committee on Research Laboratory.

The question of method of choosing a head for the laboratory was discussed.

Two active and four associate members were elected.

It was decided to hold the next Council meeting on Friday instead of Saturday.

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## PRESIDENT'S ADDRESS.*

*By Louis E. Levi.*

GENTLEMEN: The swan song of an officer of the Association about to retire to the activities of a regular member, should not be accompanied by the solemn music usually composed in those harmonies which tend to place a gloom and sorrow upon the one about to take his place in the silent halls of membership, but the enlivening strains of a patriotic march should take its place to help him do his duty towards the Association in the furtherance of its interests.

Spurred on by these martial strains of "Association welfare," the column of workers, with the flag of the confederation flying in the breeze at its head, pushes its way through the dark forests of inactivity into the clearing. When the sun of success shines upon all of us and warms the heart to quicker action, then and only then can an officer who has been honored by his confreres say—"My work is finished—I can retire."

Many a time have we passed an heraldic emblem upon which were blazoned these simple words—"Suum Cuique." We have looked time and time again at this old Latin inscription without much thought or further consideration, yet when analyzed these few words open to us new thoughts.

In the embryonic stage of our present prosperous organization, we were struggling to form a nucleus around which the stars of the leather industry could gather with the hope that the astronomers of future generations would point their telescopes of criticism towards the new constellation and place in the firmament of most useful and beneficial societies, the A. L. C. A., as a star of the first magnitude. At that time the associate members came as a solid phlanx, shoulder to shoulder, and placed us in the constellation—never to be erased. The translation of these heraldic words, as you know, is—"To each one, his own."

How calm and inoffensive these long neglected words appear. Undisturbed by the ravages of time and yet full of life when the quixotic touch of an interested person takes them down and handles them with the care due their age. They seem to speak and cry out for their application to right and wrong. Have we

* Read at the Atlantic City Meeting, June 1, 1916.

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lived up to these words? No! Has the associate member had a voice in these meetings? No! Are we to go on in this manner, doing most great injustice to those who have made it possible for us to take our place in the front ranks?

The By-Laws, Section 7, reads:

"The Association shall consist of Active and Associate members, the latter having all the privileges of the Association except that of voting."

The section should be changed so as to read:

"The Association shall consist of Active and Associate members, the latter having all the privileges of the Association except that of voting on questions of methods of analysis."

When this is done we will have paid our debt of gratitude to those who gave us a helping hand at the time it was most needed. The words upon the heraldic shield will then stand forth in the brightness which vies with the sun to give us pleasure and the associate member will have come into his own.

In order to lighten the burden of the Secretary, and make his position one of joy, with just enough work to keep him in proper form, I would suggest that Section 20 of the By-Laws be changed to read as follows:

"These By-Laws may be altered or added to at any annual meeting by a two-thirds vote of those present and voting. Written notice of proposed changes must be given the Secretary at least three months prior to the annual meeting, and he shall cause the proposed change to be printed in the JOURNAL one month prior to the annual meeting. Any member unable to be present may send his vote to the Secretary, who shall cast it at the annual meeting."

The suggestion for this change is not only for the purpose of the conservation of the funds of the Association, for the purpose of lightening the work of the Secretary, but also to make our JOURNAL the clearing-house for all business which properly comes before the members.

Before I close, let me say a few words in reference to the Research Laboratory, which you are aware is being pushed to realization. A new epoch is about to open upon the leather industry in this country with the beginning of the Research Lab-

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oratory, which the tanners of the United States are about to endow.

Original tanning research which has so long been dormant in this country is about to heed the magic wand of science and awaken to strenuous work. It behooves all of us to extend the helping hand to him who is to be the leading spirit in this old, yet, ever new, field; to give him the desired and ever welcome applause when he appears before the footlights of the theatre of science and to look lightly over the mistakes to which non-infallible man is heir.

In closing, let me thank the gentlemen of the Association for their hearty co-operation and for the great honor conferred upon one who has striven to merit your well wishes and extend at the same time, the "Salve" of the next President of the A. L. C. A.

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## CURE AND DISINFECTION OF HIDES.*

COMMITTEE REPORT, 1916.

*By C. R. Oberfell, Chairman.*

The Tariff Act of August 5, 1909, provided that importations of neat cattle and hides of neat cattle shall be prohibited excepting from countries which the Secretary of the Treasury shall declare will not tend to the introduction or spread of animal diseases. Accordingly the Department, Division of Customs, issued a circular No. 23, May 2, 1910, regulating the disinfection of hides. Since this time various exceptions and additions to these regulations have been made.

The National Association of Tanners have had a committee in close touch with the Federal authorities during this period since 1910, and part of this committee is represented on the committee of this Association.

It is an unfortunate condition that there is a popular idea regarding the prevalence of anthrax, which is erroneous, while as a fact anthrax is perhaps the least prevalent or deadly of occupational diseases. This idea is partly responsible for the drastic nature of the Governmental regulations which are working hardship on certain branches of the industry.

* Read at the 13th Annual Meeting of the American Leather Chemists Association, Atlantic City, N. J., June 2, 1916.

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In 1913 J. H. Yocum presented to the N. A. T. a paper on the disinfection of imported hides showing the relative merits of the methods permitted by the Government. His recommendation was for the use of a solution of bichloride of mercury, 1-1,000, in a saturated sodium chloride solution for green salted hides and the Seymour-Jones method, bichloride of mercury, 1-5,000 in a 1.0 per cent. formic acid solution, for flint dried hides. At the present time the Government requires a soaking for 48 hours in a 1-1,000 bichloride of mercury solution, or 48 hours in a solution of 10 per cent. sodium chloride and 2 per cent. hydrochloric acid. This latter is the Schattenfroh method.

Tanners who have tried these processes have told this committee that the Schattenfroh method is positively injurious to hide and that the 1-1,000 bichloride of mercury solution is burdensome in the point of cost. It might be mentioned that the regulations now allow the use of these methods at the tannery under Government supervision.

The N. A. T. undertook a detailed study of the whole situation and through a questionnaire sent out to the industry collected statistics as to the frequency of anthrax infection as compared with other diseases and the fatalities from same. The questionnaire was as follows:

1. How many imported hides and skins did you use during 1915?
2. How many cases of anthrax have you had in your plant during the past ten years? Report for each year.
3. For each case report: date; department in which it occurred; kind of material causing the infection; duration of sickness; treatment; whether cured or fatal.
4. How many animals died of anthrax in vicinity of your tannery during last ten years?
5. For each case of animal infection give details showing: date; location of pasture causing the infection; how did pasture become infected; were the infected areas widely scattered or confined to one small locality; was death by anthrax scientifically proven or only assumed?
6. Do you know of methods of treatment to render anthrax infection in humans reasonably non-fatal?

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7. Do you know of adequate measures for rendering cattle immune from anthrax?

The following statements are substantiated by the authorities quoted and they deserve wide publicity.

1. Anthrax has existed in this country for more than a century. The soil in a few districts of small area is apparently infected with anthrax. Some of this infection is probably due to tannery sewage, some has no relation to hides or skins or tanneries.

2. Proper regulations regarding the disposal of the bodies of animals that have died of anthrax and proper cultivation of the soil will, in most cases, make sanitary an infected district.[1]

3. Where an infected district is low land subject to frequent overflow, it is more difficult to effect sanitary conditions in the soil and in such territory cattle can be rendered immune by vaccination, at very small cost. This is done on the low lands bordering the Delaware River, the only place where anthrax among cattle has been of serious importance where tanneries could be suspected of causing the infection.[2]

4. There is no evidence indicating anthrax to be increasing in this country. The total number of deaths attributed to anthrax in New York City during the past five years is exactly the same as for the previous five years.[3]

5. Total number of animals dying of anthrax annually in the United States is insignificant compared with the deaths from other diseases. In Pennsylvania, only 15 animals died of anthrax during 1915, while in the same period 1,901 animals died of tuberculosis. In Massachusetts for the last ten years the figures were 73 to 13,090, while in Michigan there were during the past three years 1,422 cases of tuberculosis with no anthrax cases reported.[4]

6. There is no danger of widespread or serious infection of cattle by anthrax due to the operation of tanneries. The record of the three principal tanning states given in No. 5 is proof of

[1] Agricultural Dept. Bulletin No. 340. December 1915.

[2] Agricultural Dept. Bulletin No. 340. December 1915.
Letter from Delaware State Livestock Sanitary Board. March 16, 1916.

[3] New York City Health Statistics.

[4] Letter from Penn-State Livestock Sanitary Board. March 16, 1916.
Mass. State Statistics (trans. by Dr. Howard).
Mich. State Sanitary Com. letter to

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this contention. It seems impossible for anthrax to become epidemic in this country.

7. In districts which become temporarily infected, the tanner is held responsible for the occasional loss of animals due to anthrax and the evidence indicates that under the usual State and Federal supervision, the loss does not go beyond the first cases.

8. Fortunately both rinderpest and foot-and-mouth disease germs are very sensitive to exposure and cannot endure high temperatures or sunlight for long periods. These germs are also easily destroyed by germicides. Disinfecting solutions that will not kill the anthrax spore are effective with foot-and-mouth and rinderpest germs.[5]

9. Rinderpest has never visited this country. Rinderpest bacilli are very easily killed by exposure to sun and air. The fact that a hundred million hides and skins are imported annually, that these importations have continued for a century and during all this time there has been no rinderpest here, seems sufficient evidence that this disease cannot live under conditions in curing and shipping hides.[6]

10. There have been six outbreaks of foot-and-mouth disease in this country. In two of these the disease was imported by infected vaccine virus, in two from infected cattle and in the last and by far the most serious attack the cause has not been located. The Bureau of Animal Industry made a very careful investigation and is unable to locate the cause. Their report states that hides were not even "remotely incriminated." (Bull. No. 2-1915, U. S. Livestock Sanitary Assn.)

11. Undoubtedly, as foot-and-mouth disease is quite common in foreign countries and at all times prevalent in some, many of the billions of hides and skins imported into this country have come from infected cattle. Yet hides have never been accused by any one in authority of bringing the infection here. The deduction seems inevitable that the foot-and-mouth disease germ

[5] Department Agriculture Regulations allow bichloride of mercury solution 1-5,000 for 24 hours for foot-and-mouth disinfection against 1-1,000 for 48 hours for anthrax.

[6] Oral statement of Dr. Mohler of the Agricultural Dept. to Mr. Wallin.

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cannot endure the exposure incident to drying and shipping of hides and there is no danger of infection from this source.[7]

12. No cases of anthrax have been connected with the glue factories using the fleshings taken from the hides worked in the tanneries of this country and neither has there ever been anthrax in or about the various plants that handle the cattle and goat hair taken off in the tanneries. This is conclusive evidence that after the hides have passed through the liming process, anthrax germs, if not destroyed, are rendered innocuous and there is positively no danger of infection after the hides have entered the limes.[8]

It is our understanding that there is no disinfection requirement in any of the principal hide importing countries of Europe. This information is furnished by Boutcher, Mortimore & Co., Liverpool, letter of 2/29/'16, Alphonse Weil & Bros. of New York and Paris, letter of 2/17/'16, and J. H. Rossback & Bros., New York and Brazil, 2/17/'16. All these firms are very familiar with the business of hide importations into Europe.

Dr. F. W. Tilley[9] in the summary of a Bacterial Study of Methods for the Disinfection of Hides Infected with Anthrax Spores states:

> "The strength of disinfectant originally recommended by Seymour-Jones (mercuric chloride, 1 to 5,000, plus 1 per cent. of formic acid) was not found to be efficient, even without neutralization of the disinfectant. A lower dilution, 1 to 2,500, plus 1 per cent. of formic acid, was found to be efficient where no neutralization was attempted. The latter strength was not sufficient, however, to prevent fatal infection of guinea pigs by disinfected material when the disinfectant was neutralized by a 1 per cent. sodium sulphide solution three or four days after the completion of the process of disinfection. No infection was caused by the inoculation of material which had been kept a week or more after disinfection. It seems, therefore, that the Seymour-Jones

[7] Official Dept. Statement.

[8] Letter Illinois Leather Co. to Mr. Wallin. April 8, 1916.
Letter Keystone Glue Co. to Mr. Wallin. April 11, 1916.

[9] J. Agri. Research, IV—No. 1. Apr. 15, 1915 and J. A. L. C. A. IX, p. 131.

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method might be employed with dilutions of mercuric chloride, 1 to 2,500, plus 1 per cent. of formic acid, provided the treated hides are not to be subjected within a week or two to the action of any substance which will neutralize the disinfectant. This would be the case, for instance, if hides were disinfected at foreign ports before shipment to this country.

"(2) *The Schattenfroh Method.*—Hydrochloric acid and sodium chloride in the proportions of 2 per cent. of the acid and 10 per cent. of the salt and with 48 hours' exposure have proved efficient in every instance. Consequently from the bacteriological standpoint the Schattenfroh method seems to be entirely satisfactory. This conclusion is supported not only by this work but by the exhaustive researches of Gegenbauer and Reichel and Hilgermann and Marmann. The recently published work of Sevcik is not so favorable to the Schattenfroh method as that of the investigators previously mentioned. He finds that complete disinfection can be accomplished when the hides worked with are thin. But when the hides are thick and heavily infected, he was able, after very thorough neutralization, to extract from pieces of the treated hides anthrax spores which were virulent for mice, and in some instances for guinea pigs, even after exposure to a solution of 2 per cent. of hydrochloric acid plus 10 per cent. of sodium chloride for 7 days.

"Although in view of the above-mentioned results the Schattenfroh method can not be regarded as perfect, it nevertheless seems to be far superior to other methods and well worth a trial as a standard method for the disinfection of hides."

The suggestion has been made[10] that a solution of bichloride of mercury, 1-5,000 or possibly 1-10,000, when used as the preliminary soak in the tannery for 48-96 hours, and followed by the regular liming process, will prove effective in rendering the anthrax spores innocuous. From the fact that no cases of anthrax have ever been connected with the glue factories using material taken from hides which have been "limed," likewise the plants which handle the cattle and goat hair, it seems probable

[10] Letter Dr. Levy to Bureau of Animal Industry, Apr. 18, 1916.

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that for all practical purposes, this treatment might be relied on to prevent infection of workmen, and quite likely that the soak water from material so treated would not convey infection to animals. If, after further investigation, this proves to be a fact it will adequately meet the situation and relieve the tanners from undue burden or cost.

## Discussion.

T. J. Mosser: I should like to ask Mr. Oberfell if the Committee have any figures on the cases of anthrax among the men. The employers generally do not want to give these. One of the questions that was asked was how many cases they had had last year.

C. R. Oberfell: From the same tanners, covering a period of ten years—this is the statement of the National Association of Tanners—including 1915, there were 92 cases in 19 tanneries. In 62 tanneries there were no cases at all. There were 9 fatalities occurring in 7 tanneries. Out of 92 cases there were 9 fatalities, over, approximately, ten years.

In answer to a question, Mr. Oberfell said that he did not know whether cases of anthrax occurred less frequently in tanneries where lime is used for unhairing than in those not using it.

V. A. Wallin: I do not believe there was any investigation as to the method of removing the hair.

R. W. Griffith: I think the point here is whether the men handling the hides as they come in are apt to be infected, or whether at a subsequent stage of the tanning.

V. A. Wallin: I think I am correct in saying that there has never been a case—at least we do not know of any cases—where men have been infected that worked beyond the beam-house, and the probabilities are that every case was contracted by men handling the hides before they went into soak.

R. W. Griffith: Have you figures on the men infected with anthrax as to whether that included or excluded wool sorters?

V. A. Wallin: These figures have included only tanneries handling hides. We have, however, all the deaths in New York City—I think we have all the figures for New York State—but at any rate we have all the figures for New York City, and of

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course these are not alone among the tanneries. They might include the wool sorters or any industry. In fact, it is believed that some deaths in New York City came from the wearing of cheap furs that were made from cat skins.

C. BEYE: We have authentic figures which show that for the year 1915, from a census of the United States, in two-thirds of the United States there were 19 deaths all told, from anthrax.

L. BALDERSTON: In regard to Mr. Wallin's statement that the disease is probably due in nearly all cases to infection received from the hides before they went into soak, I think it should be qualified a little in the case of sweat tanneries. I know a man who had anthrax a year or two ago, whose chief business it is to watch the hides in the sweating process. He does not handle the hides before they go into soak. It seems very likely that he got the germs from the hides in the sweat pits. The sweating process is particularly favorable to the development of anthrax spores present in the hides, and the pits themselves and the earth about them have in some instances been found to be infected.

C. R. OBERFELL: So that there may be no wrong conclusions taken from Dr. Balderston's statement, I will ask him if the hides were soaked in any disinfecting solution.

L. BALDERSTON: The soaks were simply salt soaks.

C. R. OBERFELL: Of course you would not expect the salt soak to kill the anthrax spore, so that if the liming of the hide has nothing to do with the rendering innocuous of the anthrax spore, the hides going into the sweat pit would still carry the infection. It might occur there just as well as in the soaks.

F. J. NORRIS: I might say that in the past ten years we have had three cases of anthrax, and in each case the man infected was employed in our warehouse, and I do not believe you can become infected after the skins leave the soak baths. I refer to the raw skin warehouse.

R. W. GRIFFITH: That was on goat skins, wasn't it?

F. J. NORRIS: In all three cases the men worked on horse hides. We have never had a case on goat skins. One resulted fatally, the other two we pulled through.

R. W. GRIFFITH: They were infected before the skins went into soak?

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F. J. NORRIS: Before they went into soak. I do not think that after they come out of the soak, whether you put them into lime or sodium sulphide, you can contract this disease. In fact we never have had it in the past ten years.

R. W. GRIFFITH: Were they domestic or foreign hides?

F. J. NORRIS: We handle both, and it is a hard proposition to say whether it was contracted from domestic or foreign. We have never had any cases on goat skins, however.

R. L. MOORE: I know of two cases, one in a sweat tannery and the other in a tannery using a sulphide lime process, where beam hands contracted the disease, and in neither case did the men handle the hides until after they were through the liming process.

R. W. GRIFFITH: What kind of hides were they?

R. L. MOORE: Dry China hides.

V. A. WALLIN: Were these men cured?

R. L. MOORE: Yes.

V. A. WALLIN: Were they seriously infected?

R. L. MOORE: Yes, one of them very seriously. I think if you will look up the statistics of the report just read you will find that where fatalities did occur, it was in cases where proper treatment was not given to the persons infected.

F. J. NORRIS: We had one case where the physician knew but little about anthrax. Since we have employed our own physician, we have cured both cases. Before that time the fatality occurred.

C. BEYE: It is also well known in medical circles that men with weak constitutions often succumb to disease when they would not if they had normal constitutions; men that drink excessively, for instance. We had two or three cases of that kind reported, where the men were heavy drinkers and death occurred.

L. BALDERSTON: I heard a case described that might interest you. The physician who told me the story had been called in to see a man and found him suffering from anthrax. The physician who had been treating the case was present. My informant saw several marks of the hypodermic syringe about the pustules, and asked what had been injected. The other physician replied that he had given several injections of mercury bichloride. He was not able to say exactly how much had been given, but the man died of bichloride poisoning.

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F. J. NORRIS: Our physician when he starts looks for anthrax on the neck. It usually appears on the neck in the form of a small pimple. He makes five or six incisions around this pimple and injects pure carbolic acid, and afterwards resorts to the anti-anthrax serum, and in both cases has been successful. In the last case the man infected lost 25 pounds in about six days.

R. L. MOORE: Out of half a dozen cases of which I know definitely, the disease was treated similarly in each case. The infected part was cut out, and the patient was then given serum treatment.[1] In every case where the patient was taken care of by the physician in charge, the cure was absolute. In the one case which proved fatal, the physician in charge was away, and a long automobile ride was necessary to reach the nearest hospital. On being refused admission there, the patient was taken on an all-night trip to the nearest physician who was acquainted with the disease. Although he was in fair condition, it was too late to save the patient. He was a drinking man.

V. A. WALLIN: I should like to refer to three cases which we had in Grand Rapids as illustrating the ignorance of the average physician regarding this disease. In the first case which occurred, the man had this sore on his neck and had neglected it, and did not report it as he was under instructions to do. The physician who looks after our accidents took him in hand, reported that he had anthrax and would be dead the next day. I found a physician in the city who had had a great deal of experience in China, and I went to him to see if he had had anthrax experience. He said that he had, and went after the man and took him in hand and the man got well. Since that, this man has treated all of our cases. We have not lost any, but we have had four cases in the last five years. His treatment is more simple. He applies hot poultices, after slashing the wound, of salt and camphor every hour. He just keeps renewing them every hour. We put two nurses on and keep right after the patient.

This is all very interesting, but I am afraid it would lead us away from what the Committee would like to present. That is,

[1] A letter from Mr. Moore, dated Elkland, Pa., June 19, has the following passage, "Our physician here, Dr. Frisbie, has authorized me to state that he has secured excellent results in anthrax cases by the use of liberal doses of quinine along with the serum treatment. In no case were any bad effects noted".

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the idea that this anthrax danger is a very slight danger. We get interested in some poor fellow with a great sore on his face and neck who we fear might die inside of forty-eight hours, but we should bear in mind that the total number of human cases is insignificant compared with other occupational diseases, and we should bear in mind also that the number of cattle destroyed is of no importance as compared with other cattle diseases. So it seems to me that from the tannery standpoint the danger of infection is a very slight danger, and that the danger and trouble that does come is to the tanner. He is of necessity compelled to assume the burden. He has to pay for treating these patients. He has to pay for the dead animals.

There is no serious danger from anthrax. If there was a serious danger we would have had this trouble in the century we have been importing hides into this country. So it seems to me—I do not like to press the Bureau of Animal Industry at all—but it seems to me that in the matter of anthrax, leaving these other two diseases out of consideration now, that in the matter of anthrax they are going far beyond anything that is justified, because it is an economic matter entirely. They are going far beyond what is justified in trying to locate the very last poor anthrax spore that may be hidden in the interior of a hide and finding a disinfectant that will swell him up, root him out, plump him up and kill him. You might just as well say that nobody must ride in automobiles because automobiles have killed people. I think the Government is going too far in making a great deal of this anthrax danger.

As to the other two diseases, they are serious. When they come, they spread like wild-fire. They go all over the country in no time if they are not immediately headed off. But fortunately a very mild disinfectant will knock out rinderpest and foot and mouth disease. Rinderpest has never been in this country, and if it has not gotten here in a hundred or more years, it seems safe to conclude that it will never get here.

Still, I think the tanners, in order to make assurance doubly sure, would be willing to adopt as a safeguard against this remote possibility of rinderpest and foot and mouth disease a disinfecting solution which could be used as a first soak in their tanneries. It would cut off this very remote possibility of rinderpest and foot

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and mouth disease coming from the tannery, and it would probably go a long way, at least, toward cutting off the danger of anthrax to the tanner, because the trouble is confined generally to the tanner. He has to assume that danger. It seems to me that a solution of one to ten thousand of bichloride of mercury—if the hides are put into that solution as long as from four to five days, which is possible in the case of hides, and a shorter time in the case of skins, that ought to be ample, and that it ought to insure 99 per cent. of the danger, and that it ought to insure all of the danger from foot and mouth disease and rinderpest. I wish Dr. Tilley, just from a scientific standpoint, would tell us what a one to ten thousand solution would do in the way of rendering us safe from these three diseases.

R. W. GRIFFITH: I take it, Mr. Wallin, that another point that the Committee would want to bring out is, that cases of anthrax, if they are diagnosed and treated in time are not necessarily fatal.

V. A. WALLIN: Since this new serum has been pretty well known and adopted, the Mulford serum, which I believe the Bureau of Animal Industry was largely instrumental in perfecting, there ought to be none of the cases lost. I think it would be very desirable to have the various tanneries arrange to have some of that serum in hand. I understand that after it gets so old that it ceases to be potent it can be exchanged, and the cost of keeping it on hand at every tannery would not be very serious.

R. W. GRIFFITH: Is it very difficult to identify the disease?

V. A. WALLIN: I think not. It has such a peculiar, angry appearance that you can safely say it is easily identified.

R. W. GRIFFITH: It may be identified in its early stages?

V. A. WALLIN: Of course we ought to take the necessary precautions. If a man has a little scratch or a little wound and is working in a tannery, that ought to be disinfected on general principles. There was a peculiar case in Sheboygan. They are very careful in the tannery there, and the men working on China hides were instructed to change their clothes. They had caps and gloves and so forth, and were instructed to change them. The particular man in question disregarded this rule, and he went to

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his home with these clothes on and took his little child in his lap. The little child had a scratch of some kind and got infected from her father's clothes. They took the child in hand, however, and saved her.

L. E. LEVI: Speaking about this case, the case turned out to be measles.

A. H. LOCKWOOD: I think that there is one point that it will be well to refer to here. It seems to me that I may be excused for saying this, as my business is publicity. The departments of the Government are influenced a great deal by public opinion. The daily papers and magazines live by creating it and pandering to it. They like to print "human interest stories." The daily papers and magazines care nothing about technical matters such as we are discussing. They want something sensational. They want a man with an angry sore on his neck and in 48 hours he is dead. That's great! That's news! That's human interest! The result is that we have wide publicity about anthrax, and the great American public has no doubt that anthrax is a horrible, deadly disease, that it is malignant and is going all over the country. And the sensational part of it is just what the newspapers want.

V. A. WALLIN: In our case they had headlines in the papers.

A. H. LOCKWOOD: Yes, they have headlines. This must be counteracted by creating sane, healthy public opinion, and I must say that the trade papers have not been allowed to print matters that I have regarded as of the very greatest importance to help in engendering healthy public opinion with regard to anthrax. The National Association of Tanners, some months ago, had a long array of matter pertaining to anthrax, and I begged and prayed for permission to print it in the *Shoe and Leather Reporter,* but was not permitted to do so. I just want to say that publicity, sunshine and daylight, are great disinfectants and great correctors of the wrong idea the American public has in this matter.

L. BALDERSTON: It is true that there is not much anthrax about, but it is also true that it is a horrible disease. Anyone who has seen a case of it, does not want to get it, and does not want to subject his employees to the danger of getting it. Now, while

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any suitable process of disinfection takes care of the hides after they come out of the soaks, what about the hides before they go into the soaks? Let us take care of the men who handle them before they go into the soaks. I have seen a great deal of the handling of hides, and in the majority of instances the proper precautions are not taken. For instance, the man who handles the hides will not wear a respirator. Anthrax does not always come through infection from a scratch or small wound. It can come in other ways. A man can inhale the spores and contract wool sorter's disease. Let us use the proper precautions. It does not scare men to death to provide them with the proper means of avoiding dangers. Let us provide the proper means and use proper precautions to prevent danger in handling dry hides before they go into the soaks.

V. A. WALLIN: That is the most dangerous place.

R. W. GRIFFITH: Has the Committee any recommendations to make with regard to the methods of handling dry hides?

C. R. OBERFELL: Not in this report. That may come after the discussion, which we hope will bring out some of these points.

L. BALDERSTON: It seems to me that a proper precaution, besides the use of gloves, would be some kind of a disinfecting lotion or ointment that could be put over the face and neck, and then a respirator worn. This I think would be the most complete precaution against contracting the disease, because the germs nearly always get in through scratches. If there was something on the skin to catch the anthrax spores and kill them as they light, it might protect the men.

F. J. NORRIS: It is an impossibility to get the average laboring man to do that. We have tried our level best to protect our men in the warehouse. If a man has a scratch or a pimple we send him over to our hospital to have the sore disinfected. We also provide gloves and respirators; and the men will not leave them on. They think the respirator is a nuisance and throw it aside. As long as the foreman is standing along side of them they will wear it, but as soon as he turns his back, off goes the respirator. We also provide pails of bichloride of mercury for workmen to wash their hands before eating. Some of them use it, and some

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do not. You say, "Discharge a man, if he fails to live up to your rules," but I want to say that it is a pretty hard proposition to get men to take their places who will do it.

R. W. GRIFFITH: Dr. Levi, can't you tell us of some of the precautions you are taking?

L. E. LEVI: The gentleman who has just talked to you has stated all that we do. We provide the men with respirators and they are obliged to wear gloves, and all the dry hides that we get are disinfected.

V. A. WALLIN: How are they disinfected?

L. E. LEVI: We either use lime or a one to five or one to ten thousand bichloride of mercury solution—mostly one to ten thousand. The Bureau of Animal Industry, I believe, recommend a 3 per cent. cresol solution, but we do not like it on account of its inefficiency. They say 3 per cent., but with a 10 per cent. solution we find it will not kill the bacilli in twenty-four hours. A 60 per cent. solution will not kill the spore. Now, if there is a spore there, the cresol solution is worthless. We prefer to use bichloride of mercury because it will absolutely not damage the hide in any way, shape or manner. About ten years ago, when we started to disinfect our dry hides, we made an experiment with bichloride of mercury salt, mixed with five or ten times the amount of common salt. We spread this over the hides or skins as thickly as possible, then sprinkled with water, and let these skins remain in that condition for about thirty days. We took these skins and put them through the tannery and found that the skins were not damaged at all. We do not use the cresol products, which are liable to contain a goodly percentage of carbolic acid, because we found that carbolic acid has a certain tanning effect on raw stock and prevents the hair from coming off.

V. A. WALLIN: May I ask you—I think you are using a one to ten thousand solution as a soak—what determination have you made that this is efficacious as a disinfectant for anthrax?

L. E. LEVI: We only had one case. We take a sample of all the hides that go into the soaks and test them bacteriologically and we have only had one case where our bacteriologist thought he found anthrax bacilli.

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V. A. WALLIN: After the soaking?

L. E. LEVI: Before the soaks. We took the hide on which he thought he had found the bacteria and marked it and put it through, and when it came from the limes he got absolutely no bacteria at all. This is the only case we have had where he thought he had bacilli.

V. A. WALLIN: And yet you knew you had anthrax before it went into the disinfecting solution?

L. E. LEVI: Yes—he thought so, either B. anthracis or B. subtilis (pseudo-anthracis). But it is very easy for a bacteriologist to get mixed up. He did not go far enough into it so that we could say positively that it was anthrax bacilli. That is the only case we have ever had. After it came out of the lime liquor, there was absolutely no trace.

V. A. WALLIN: But you have known positively that you have had anthrax bacilli on the hides before they went into the soaks?

L. E. LEVI: We thought so, and so to be sure of it, we marked that hide and put it through.

V. A. WALLIN: I mean on other hides, do you frequently find anthrax bacilli before they go into the soak?

L. E. LEVI: No, we do not. Only in that one case. We have not had a case there in Milwaukee in forty years.

W. H. TEAS: How do you disinfect the hides before taking them out of the cars?

L. E. LEVI: We spray them. We spray them as the Bureau of Animal Industry recommends. We use spraying machines. They are sprayed each time—opened and sprayed again.

C. BEYE: I understand that your company discipline their men in the observance of your rules and regulations by discharging them if they do not abide by them. Is that correct?

L. E. LEVI: That is correct.

C. BEYE: That policy is followed by several large companies, and while it would be rather a hardship on the tanner under the present labor conditions it is the policy that ought to be followed.

L. E. LEVI: When we handle the cars there are probably ten or fifteen men there, and we have a foreman who does nothing else but see that they carry out all precautions required by the firm. We had a hard time to get the men to wear respirators—

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we found they did not want to do it. The sponge in the respirators would get dry, so we have them moisten it often with salt water.

C. R. OBERFELL: It might be well to bring out another point. I think it has been amply shown that the danger of infection in humans is comparatively slight, but there is another side to it, and that is the infection or possibility of an epidemic of anthrax amongst animals—cattle and horses. I think there has been more pressure brought to bear by the various live stock associations, to prevent an epidemic among animals than there has been pressure brought to bear to prevent an epidemic among human beings.

It has been found out by the Delaware Live Stock Sanitary Board that there is an absolute safeguard against the spread of anthrax, that is, by vaccination, and it has also been found that anthrax is not a virulent disease among animals and cattle and does not spread like foot and mouth disease.

R. W. GRIFFITH: As this discussion is proceeding along scientific and bacteriological lines, it might be well to call upon Dr. Tilley of the Bureau of Animal Industry to read his paper on the Cure and Disinfection of Hides.

F. A. TILLEY: I have no paper prepared. Nothing was said about a paper. While listening to the discussion I have noticed some things about which I should like to make a few remarks. In the first place, it seems the question is mostly whether anthrax is as serious as some people say it is, or whether it is not. Of course, as Mr. Oberfell has said, anthrax is not, relatively speaking, a very virulent disease. I do not think the officials of the Bureau hold the view that the danger to be feared is an epidemic of anthrax, but rather a steadily increasing spread to new localities.

I note that the report which Mr. Oberfell read says that infection of the soil to any serious extent exists only along the Delaware River. Some instances have come to our attention of extensive infection of the soil around tanneries in New York and also in New Hampshire. I believe in one case suit has been brought against a tannery on account of alleged damage to the soil.

Another point; I noticed that one man spoke of the absence

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of regulations in various European countries as compared with what are thought very strict regulations of our Government. Of course, it might be said that anthrax and foot and mouth disease and a number of other diseases are more or less endemic in these other countries, and perhaps you might say it would not matter whether they made extensive regulations or not. But, fortunately, in this country, foot and mouth disease and rinderpest do not exist, except the foot and mouth disease very rarely; and of course anthrax is endemic in this country in some restricted localities, but comparatively speaking is very rare, and from that standpoint it would seem very desirable that we take all possible precautions to prevent its spread.

If I might say so, it seems to me that possibly some of the gentlemen have rather underestimated the prevalence of anthrax and its seriousness. Some of you have made remarks about the ignorance of physicians in regard to it. If that is true of the physicians, it is safe to assume that the general public are still more ignorant, and it is quite possible that a great many more cases of anthrax exist than come to our attention.

Mr. Wallin said something about a 1 to 10,000 bichloride solution. I should think that bichloride would be all right to use that way in various strengths, provided the hides were left long enough after the treatment with bichloride. A peculiar thing about bichloride of mercury is that it is extremely slow of action. For instance the bichloride and formic acid of the Seymour-Jones method takes something like two weeks to destroy anthrax spores. So, I should say, perhaps a 1 to 10,000 might be effective if you allow long enough time and do not neutralize the bichloride right away. Certainly for a short time the combination between the bichloride and the spores is what we might call a "reversible" combination, and the effect of the lime will be to break the combination, and the spores will, so to speak, come to life again.

V. A. WALLIN: Dr. Tilley, may I ask you before you finish—has there been any test made to determine what is the relation between the length of time and the strength of the solution? I think Dr. Hickman told us yesterday that the requirement in preparing hides for export at the point of origin is the 1 to 1,000 bichloride of mercury solution for 30 minutes. Now, would the 1 to 5,000 solution, say, for 48 hours, or the 1 to 10,000 for

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96 hours, be as effective as the 1 to 1,000 for 30 minutes. Were any data gathered on this point?

F. A. TILLEY: In the stronger solutions the effect would be obtained in shorter time. For instance, with a 1 to 2,500 bichloride solution and formic acid, the combination between the spores and bichloride apparently is permanent in about 10 days, and if you use a 1 to 4,000 solution, it is not permanent in that time, but takes nearly three weeks. I do not know whether that answers your question or not.

V. A. WALLIN: Yes, that has a bearing; but you have not just established a relation between 4 days or 2 days and 30 minutes. Do you know which would be the more effective, say, 1 to 5,000 for 48 hours, or 1 to 1,000 for 30 minutes.

F. A. TILLEY: I should say probably the weaker dilution and the longer time, because bichloride has a very superficial action unless you allow it time to soak in.

V. A. WALLIN: I think if the tanners were to use this material as a soak—they could soak skins at least 24 hours, and hides they could soak probably 4 to 6 days. At least, the minimum they could soak would be 4 days.

F. A. TILLEY: That is, the 1 to 1,000?

V. A. WALLIN: Well, particularly the 1 to 5,000—for two reasons, as a matter of expense, and also because there has been some complaint among the employees against handling the hides that have been soaked in a 1 to 1,000 solution. There is a feeling that there is some danger of bichloride of mercury poisoning. I do not know how just this is. I cannot speak with assurance.

F. A. TILLEY: To refer to some experiments of my own, the 1 to 1,000 solution would hardly be of much use against anthrax. This seems to be a bone of contention.

V. A. WALLIN: I think we admit that is so. All the evidence seems to prove that the 1 to 1,000 is not sure death to anthrax.

F. A. TILLEY: We have recently tried it out for as long as a week, and the anthrax still lived.

V. A. WALLIN: Was that on spores that were fully exposed?

F. A. TILLEY: No, on spores on the inside of the hide.

V. A. WALLIN: Bearing in mind that we can find no case of anthrax in the glue factories that handle the fleshings, or in the Illinois Leather Company's hair plants scattered over the United

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States (and this company handles 75 per cent. of the hair taken off in this country), it seems pretty conclusive that they cannot endure past the lime process. If this is the case, is it of any practical importance to kill the spore which is in the hide? I do not mean to commit you or the Department in this matter, I merely wished to talk it over in a friendly way.

F. A. TILLEY: Of course, in anything that I say, I am not speaking for the Department. I am merely speaking informally on the subject.

V. A. WALLIN: It is a fact, gentlemen, that this Schattenfroh method, which involves hydrochloric acid, and which it is generally agreed is the most nearly sure death to anthrax of any, although people disagree about that, that method, from all the evidence we get, is absolutely impossible to use.

The stock gets so plump that it is impossible to get the hair off, and when it goes into the yard it is as thin as paper.

S. SAXE: Do you know anything about the disinfectant known as Chinosol?

F. A. TILLEY: From what little I know about Chinosol, I should say that it is a good antiseptic, but a very poor germicide. Some years ago, I tried Chinosol against the typhoid bacillus. I think it was a 10 per cent. solution that was necessary to kill the typhoid bacillus in 5 to 10 minutes. Of course, anything that requires so strong a solution would hardly be of very much use as a germicide.

F. A. LOVELAND: I should like to ask your opinion on this proposition. If the tanners should generally adopt a method of disinfection by bichloride of mercury, and then run the soaks into a stream, what would be the effect of that upon the fish in the water, or animals drinking from the stream?

F. A. TILLEY: I should think it might poison them. I think some states have laws on that subject.

L. BALDERSTON: We have found that the hides take out the mercury almost completely from the 1 to 1,000 solution, and from the 1 to 5,000 quite completely.

F. A. TILLEY: Some recent analyses I know of would bear that out. Samples from different places have been sent in, and I believe the largest amount of mercury bichloride found was about

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one-tenth of the amount put in, and from that down to a mere trace, just enough to say there was a little there.

V. A. WALLIN: Not enough to say it would be dangerous to the sewage?

F. A. TILLEY: Not unless there was a very large volume of used soak in the sewage.

A. ROGERS: Would not that be precipitated by the lime? In the sewage you have a lot of lime and other things.

F. A. TILLEY: I presume that would be so. I am speaking more from the standpoint of a bacteriologist.

H. C. REED: If it is true that there is a combination of the hide and the mercury, would the mercury penetrate into the interior of the hide?

F. A. TILLEY: It probably would not. It combines indiscriminately with everything in sight anyway, and by the time it had combined with everything on the outside, there would be none left for the inside of the hide.

V. A. WALLIN: The 1 to 5,000 or the 1 to 10,000 would be a sure cure for rinderpest or foot and mouth disease?

F. A. TILLEY: I would not presume to say for certain. I should say that it would probably be effective against those diseases. Comparatively weak solutions of carbolic acid and similar disinfectants are effective, and I presume a 1 to 5,000 of bichloride would be efficient; except, of course, that bichloride is very superficial in its action.

V. A. WALLIN: I do not think I understand that.

F. A. TILLEY: My comment was that the action of the mercury is superficial, and the question of whether or not disease germs are destroyed depends on whether or not the bichloride penetrated far enough to get at any germs below the surface of the hide.

F. A. LOVELAND: Would it affect the grain of the hide?

F. A. TILLEY: You will have to ask some of your chemical friends. That is a question I also should like to have some of you answer.

V. A. WALLIN: I think that our experience has been that the 1 to 1,000 is not unfavorable to the hide or to the tanning operation.

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F. A. TILLEY: Did you notice from the pieces that were sent to you that there was a discoloration?

V. A. WALLIN: The ones sent to Grand Rapids? Yes, there was a discoloration.

F. A. TILLEY: I wondered if any of you noticed the discoloration. It was probably due to the disinfectant.

V. A. WALLIN: Were they treated with bichloride?

F. A. TILLEY: Those particular ones were, I think.

V. A. WALLIN: I do not remember the particular ones.

F. A. TILLEY: As I remember, there were samples treated with hydrochloric acid, and some treated with bichloride and formic acid.

V. A. WALLIN: I do not think that I can answer. I know most of them are unsatisfactory. But in what I was saying about objection to the use of 1 to 1,000 bichloride on the part of employees, I referred to the experience which the Elk Tanning Company are having. I think the only criticism that has come from the tanner has been on the part of the employees—it either made them sick or poisoned them, or they did not like it in one way or another. But my understanding is that it does not injure the hides.

R. W. GRIFFITH: Is the Leather and Paper Laboratory collaborating with the Bureau of Animal Industry?

F. A. TILLEY: They have co-operated to some extent in the work on hides treated with hydrochloric acid and by the Seymour-Jones method. That is one reason for my question to Mr. Wallin, because the pieces Mr. Rogers showed me showed quite a discoloration.

C. R. OBERFELL: Was not that merely in the hides, and after it was tanned, was it all right?

F. A. TILLEY: The leather looked all right. Possibly it was a question of the discoloration being covered up by tanning liquors, and it may be that the discoloration entirely disappeared. Do you remember that, Mr. Rogers?

J. S. ROGERS: I do not think there was any special discoloring after the tanning was finished. These were merely small test pieces.

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R. W. GRIFFITH: Have you any observations in a general way to offer, Mr. Rogers, from the experience of your department?

J. S. ROGERS: I do not know that the experiments that we carried out are really worth consideration at the present time, for the reason that the instructions we sent were not in sufficient detail to give Mr. Wallin the proper information before he began to tan the hides. It is quite probable that the experimental hides would have given better results had the tanner been fully informed concerning their previous treatment. Of course, the tanner would have this information about hides which were disinfected by an official method.

V. A. WALLIN: We had no information as to what had been done to the hides.

J. S. ROGERS: If you had known the treatment beforehand you would doubtless have modified your method of handling.

V. A. WALLIN: In reference to the Schattenfroh method, I think Mr. Loveland has had some recent experiences which I should like to hear.

F. A. LOVELAND: This method is treating with hydrochloric acid and bichloride of mercury. We could not get hydrochloric acid and so used the formic acid method, formic acid and bichloride of mercury. We had 343 hides disinfected by that method. I was not at the tannery at the time they were disinfected. I did not see them until they were passing through the beam house, and the beam house foreman said they were very hard to flesh on account of their highly swollen condition. I saw the hides after coming out of the limes, and they looked very flat and thin. I followed them into the handlers and layers and they did not look good to me. The hides did not swell up properly, and the grain was rather rough. Just before coming here, I had 50 sides taken out of the tanning liquors and washed, bleached and dried, and I observed these against similar sides, and found that the grain continued rough, and on weighing up and getting general results on the 50 sides taken out, I should say that the gains would be from 10 to 15 per cent. low; all of which, in my judgment, would make that method impossible to use, and I would not want to try it again.

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F. A. TILLEY: Did you notice any discoloration?

F. A. LOVELAND: No.

R. A. LANG: At the time the foot and mouth disease was prevalent in Illinois, we bought hides from dealers which I believe were dipped in a solution of bichloride of mercury. I do not know the strength of the preparation, but it was to satisfy State regulations, and we noticed considerable discoloration in that leather when it came through.

C. R. DELANEY: Some men in the extract business made experiments a number of years ago in sterilization by means of a vacuum, and I have been wondering whether any experiments have been made by putting some of these hides in bales in a vacuum chamber and exhausting the air, and then introducing a germicidal vapor. This method is used in the treatment of railroad ties. There seems to be a lot of talk about chemicals. People do not like to use them. The other method, I imagine, would be far cheaper and quicker.

I do not know whether Mr. Reed can bear me out in this. We have made a lot of experiments in the sterilization of sumac extract. Sumac, as you know, would rather go bad than do anything else. We found that when it went into the vacuum chamber it was very lively, and after it came out it was absolutely sterile.

V. A. WALLIN: Would it require much heat?

C. R. DELANEY: Very little. A very good vacuum chamber could be constructed that would work on the exhaust steam. You can get the temperature in the vacuum as low as 60° F. That is, of course, very low, but you can easily get a temperature of 117° F.

It was suggested that treatment with hydrocyanic acid, which is used for disinfecting nursery stock to prevent the spread of San Jose scale, might serve to disinfect hides containing anthrax spores. Dr. Tilley replied that while hydrocyanic acid is a very good insecticide it is not an efficient germicide.

V. A. WALLIN: I think that Dr. Tilley has said that there is nothing yet discovered that will kill the anthrax spore without injury to the hide. Is that the case, Dr. Tilley?

F. A. TILLEY: At the present time I think that fully describes the situation.

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(At this point Mr. Wallin expressed the hope that the report which had been read would be submitted for criticism to the members of the Committee who had not been present at the Committee meeting. This has been done, and the report as printed above has received the approval of all the members.)

V. A. WALLIN: It seems to me, Mr. Chairman, that for the present at least, since there has been no disinfectant discovered that will positively do the work, we have got to consider it just as a practical matter from a business standpoint, and we feel quite confident that the Bureau of Animal Industry will consider that we should do at present that which will relieve the most, if we cannot entirely overcome the evil. I do not think that at this time this Association should offer any resolutions in the matter.

R. W. GRIFFITH: Have you any recommendations to make, Mr. Oberfell?

C. R. OBERFELL: Only our Committee report, after it is in final form for publication.

R. W. GRIFFITH: Will that report embody any recommendations?

C. R. OBERFELL: Well, the recommendations are based on the present conditions, that we have been able to verify by certain authorities. They are statements of fact which we have collected and we are willing to have them appear as coming from the Committee.

R. W. GRIFFITH: Would you care to speak for the Bureau with regard to the recommendations, Dr. Tilley?

F. A. TILLEY: That is really a question for the administrative officials, and I would not presume to say how they would stand on that. From the standpoint of absolute accuracy, I am afraid that bichloride would not absolutely kill the anthrax spore in every case.

C. R. OBERFELL: The suggestion has been made that the solution might be effective in killing anthrax. It is a point to be determined.

V. A. WALLIN: Your belief is, Dr. Tilley, that it would not be effective in killing anthrax?

F. A. TILLEY: I do not believe it would be under the conditions as I understand them, of immediately carrying the hides into the limes.

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V. A. WALLIN: It seems to me that the danger there is not with the anthrax that is left in the hide, but perhaps the anthrax germ or spore might be in the soak. Now I was going to ask if there is any way in which the Department of Agriculture can co-operate with some of the tanners and try this method out, say, a 96-hour soak in a certain solution, knowing that there is anthrax in the soak at the beginning, and determining whether there is any left in. Is that possible to test, or can you find them swimming around in so large a quantity as that?

F. A. TILLEY: It would be rather difficult with so large a volume of material. Along that line, commenting on the difficulty of recovering anthrax spores, there is a recent experience of ours. There were two cargoes of hides suspected of being infected. We took a large number of samples, and in the first cargo found no anthrax whatever. When we came to the samples from the second lot, with comparatively little searching we found anthrax spores present. The anthrax spore is hard to find, and it would be impossible in many cases to say whether anthrax was there.

V. A. WALLIN: You cannot identify them by looking at them?

F. A. TILLEY: In cases where I have isolated the anthrax bacillus from hides, I made a sort of extract of the hide and then examined that, but there were so many different bacteria present that it was impossible to identify the anthrax bacillus, and it was obtained only by animal inoculation.

V. A. WALLIN: Is there a certain proportion of the anthrax bacilli or the anthrax spores that would be killed by this bichloride of mercury solution? Would you be killing off a large proportion of them and still leaving a portion?

F. A. TILLEY: I do not think I have an answer for that. All that I can say is that anthrax spores vary very greatly in vitality. I presume that a great many of them might be killed off by the previous treatment of the hides, etc. At the same time, there is always danger of a certain number of virulent spores going right straight through. I am speaking, of course, on the assumption that the bichloride is immediately neutralized. As I understand it, the proposition is, to carry the disinfected hides right into the limes, and so on.

V. A. WALLIN: That is the way they would generally go. I

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should like to ask Dr. Levi whether he thinks the method they are pursuing is effective against anthrax spores.

L. E. LEVI: We have found it to be, so far We have had no cases in ten years.

F. A. TILLEY: I should like to know the source of the hides.

L. E. LEVI: China, India, and all over.

F. H. SMALL: I should like to inquire of Dr. Levi whether, after the hides are sprayed, they are so wet that it is necessary to put them directly into process, or whether they can be stored.

L. E. LEVI: They can be stored, but they have to be turned every once in so often, so that they do not get hot.

A member inquired whether the Bureau of Animal Industry had experimented with a mixture of mercury bichloride and ammonium chloride, which form a double salt that is more easily soluble in water than mercuric bichloride.

F. A. TILLEY: Such a combination, if you can call it such, of ammonium chloride and mercuric chloride is used in the so-called antiseptic tablets you buy for disinfecting purposes. That is the tablets are a mixture of ammonium chloride and bichloride of mercury. The effect would be about the same as the addition of any chloride or any acid. It might to a certain extent aid the action of the bichloride, but only to that certain extent.

ALLEN ROGERS: In New England, where they have had some trouble with anthrax, there is an interesting case between two tanneries. One tannery this spring has had five cases and two of the men died. The town was pretty well wrought up about it. That particular tanner sprays the skins. The other tanner throws the hides in salt and hydrochloric acid and, if I remember rightly, they soak four or five hours. I have seen these hides after the soaking and washing and they do not swell up.

I have been wondering in this case whether it was possibly due to the fact that in the case where the hides were thrown into water that perhaps the anthrax spores are wet down so that they cannot get away, whereas by the sprinkling process the hides were more or less thrown around, thus producing considerable dust. It was claimed, however, that they had not contracted the disease through breathing in the dust. The foreman in one of these tanneries showed me some hides which he said were infected with anthrax. I do not know anthrax, but he showed me

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little soft patches on the flesh side of the hides which he claimed were anthrax patches. It might be of interest to the Department to get hold of this fellow.

In the tannery soaking the hides, they are using hydrochloric acid, titrating, and then adding enough salt and acid to make up the loss.

Mr. Yocum and myself several years ago treated some hides by the Seymour-Jones process, and these were tanned in northern Pennsylvania—I forget just where they came from—but the idea was to see if the use of formic acid would interfere with sweating. On being tanned they came out all right, and I think there was no trouble with swelling. It seems to me that the use of salt with the acid would prevent swelling.

E. J. HALEY: Mr. Oberfell, has that Committee been in touch with the members of the Department of Agriculture?

C. R. OBERFELL: Some of the members have. Mr. Wallin has been in touch with the Department, and Mr. Beye also.

A. ROGERS: There is a material used for making surgical sutures called 'Kalmarid,' which is a combination of mercuric chloride and potassium iodide. The work done along surgical lines shows that this antiseptic is very much stronger than iodine, which had been the strongest known. It might be possible that experiments with this could be carried on, and it might be of interest to see what it would do. Of course, it is a little more expensive than bichloride of mercury, but it is very much stronger.

V. A. WALLIN: I should like to ask what value there is in a 30-minute treatment with 1 to 1,000 mercury bichloride solution, which the Department prescribes for hides at the point of origin.

F. A. TILLEY: I do not know whether I want to comment on that. (Laughter.)

V. A. WALLIN: I withdraw my question.

C. R. OBERFELL: Mr. Reed has just suggested to me that taking Mr. Delaney's idea of putting the hides in a vacuum and exhausting the air and then introducing a solution of bichloride of mercury, that the penetration there would be so rapid, that the combination with the hide substance—the mercury with the hide substance—would not be sufficient to prevent the penetration all the way through and into the anthrax spore. This is somewhat

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along the lines used in impregnating wood, putting it in a vacuum and introducing a solution which penetrates to the interior. I think Mr. Delaney's suggestion was to introduce a gas of some kind. Mr. Reed modifies that by the introduction of bichloride of mercury solution, and it may be practicable.

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## FUEL VALUE OF SPENT HEMLOCK BARK.*

By Byron E. Parks.

There was a time, not very many years ago, when the tanner cared very little about the fuel value of spent tan bark. He had a surplus, so the efficient combustion or the relative fuel value of this refuse was of little moment. They were only concerned with the problem of how to dispose of it.

Improved leaching methods and the increased use of extracts have materially reduced the quantity of bark used per unit of leather output, so that there is no longer a surplus and it is now necessary to supplement the spent tan bark with some other fuel, usually coal. This has brought home to the tanner the fact that the spent tan, which had heretofore been considered as a refuse to be disposed of, has a distinct monetary value as fuel. Also, that the question of efficient combustion is well worthy of consideration.

What is the fuel value of spent tan bark? Or, in other words, what is the relative value of tan bark as fuel, compared to the average bituminous steam coal?

To answer this question, it is necessary to analyze the bark to determine just what portion of it is available as fuel after the leaching process.

Take one cord of average air-dried bark as a basis of calculation. It will weigh, in the condition in which it comes from the pile, about 2,240 pounds, and will carry about 15 per cent. of moisture, equal to 336 pounds. The tannin content and the other matter soluble in water will amount to about 11 per cent. of the weight of *absolutely dry* bark, equal, say, to 210 pounds. Assume that leaching is carried to 95 per cent. efficiency, the tannin and

* Read at the 13th. Annual Meeting of the American Leather Chemists Association, Atlantic City, N. J., June 3, 1916.

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other solubles extracted from the bark would weigh 199.5 pounds, say in round numbers 200 pounds.

Deducting the moisture content, 336 pounds, and the solubles, 200 pounds, leaves as a residue, absolutely dry, 1,704 pounds, or say, in round numbers, 1,700 pounds from each cord of bark which is available as fuel.

Owing to the fact that each cord of bark, even from the same pile, will vary somewhat in its condition, the figures here given are intended to be average, rather than extremes either way.

Analyses made by a number of authorities vary to some extent as to the thermal value of spent hemlock bark, but probably no more than would be expected of samples obtained under varying conditions, and when this is taken into consideration the differences are very slight.

As long ago as 1875, Mr. Theron Skeel, a well known engineer of that time, made a series of carefully conducted experiments in burning spent hemlock bark, alone, in various types and proportions of furnaces. In connection with these experiments he obtained analyses of a number of samples of spent tan bark which run from 9,000 to 9,800 B. t. u. per pound of spent bark *absolutely dry.*

Analyses which the writer has obtained at various times have shown about the same B. t. u. value. Therefore the writer has adopted a value of 9,500 B. t. u. as a fair average for this class of fuel, for estimate purposes.

Spent hemlock bark, in the condition as usually discharged from the leach, the writer has found to average 65 per cent. moisture. Therefore he uses that factor in estimating the fuel value of wet tan bark. The residue, *absolutely dry,* from 2,240 pounds of bark ground, we have found weighs 1,700 pounds, carrying 65 per cent. moisture. The gross weight would be

$$\frac{1{,}700 \times 100}{\cdot 35} = 4{,}856 \text{ pounds.}$$

A pound of wet tan bark carrying 65 per cent. moisture would represent only 0.35 pound of bark *absolutely dry.* We have, then, as the thermal value of wet spent tan bark, the following:

$$9{,}500 \times 0.35 = 3{,}325 \text{ B. t. u.}$$

Now before the wet bark, as fed to the furnace, can be con-

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sumed, the moisture content must be evaporated from and at 212°, then superheated to the temperature of the escaping chimney gases, and the B. t. u. required to do this must be deducted from the fuel value of the bark as fired, in order to arrive at its net fuel value.

The average temperature of tan bark as fed to the furnace is taken at 100° F., the average temperature of escaping chimney gases at 500° F., and the specific heat of superheated steam at constant pressure 0.463. We have, then, the following:

| | |
|---|---|
| To raise the temperature of 1 pound of water from 100° to 212° will require..... | 112.82 heat units |
| To evaporate 1 pound of water from and at 212° will require ..... | 970.4 heat units |
| To superheat 1 pound of steam from 212° to the temperature of escaping chimney gases, assumed at 500°, will require..... | 133.34 heat units |
| Total ..... | 1,216.56 heat units |

1,216.56 × 0.65 = 790.76 heat units.

This would then represent the B. t. u. value that must be taken from each pound of wet spent tan to expel the moisture content. Therefore the net fuel value available would be:

3,325 — 790.76 = 2,534.24—say, in round numbers 2,534 heat units.

A good average grade of bituminous steam coal will have a thermal value of 13,000 B. t. u. per pound. Hence the relative value of the fuels would be as follows:

2,534 ÷ 13,000 = 19.5 per cent., or, say in round numbers, 20 per cent.

Cost of coal being $3.00 per ton, the relative value of spent hemlock bark would be $3.00 × 20 per cent. = $0.60 per ton.

Obviously, this value will vary with the moisture content of the bark. The writer, however, believes it to be a fair average value for spent tan bark in the condition in which it is discharged from the leach.

One cord (2,240 pounds) of air-dried hemlock bark, after leaching, will leave a wet residue having a gross weight of 4,856

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pounds. Dividing this by 2,000, we have 2.428 tons, which, at 60 cents per ton, would be $1.46, the value as fuel of the spent tan per cord of bark ground, when compared with coal of 13,000 B. t. u. value at $3.00 per ton.

Grand Rapids, Mich., May, 1916.

## NOTES ON SULPHONATED OIL ANALYSIS.*

*By W. K. Alsop and L. A. Cuthbert.*

We have read with interest the Committee Report on Sulphonated Oil Analysis published in the May JOURNAL. It seems to us that the methods of analysis advocated by some members of the committee and the final scheme proposed by the committee leave something to be desired even as a means "whereby the manufacturer and consumer can meet on an equitable basis."

There is unquestionably a lot that we do not know about sulphonated oils and our remarks are based upon what we have observed in testing numerous samples and in a measure upon the results obtained with the oils in practical use. It is true that certain of the methods of analysis are rather faulty and perhaps some of the determinations are of problematical value from a practical standpoint. The results from the use of some sulphonated oils in the tannery are sometimes somewhat disconcerting in view of the laboratory tests. However, these results should not always be taken too seriously and some considerable experience leads us to feel sure that a good sulphonated oil is better than a poor one.

We believe that, possibly leaving out of consideration the effects of different kinds of oils, one of the most important factors in the valuation of a sulphonated oil for our use, is the determination of the degree of sulphonation as shown by the organically combined sulphuric acid ($SO_3$).

It may be that the same degree of sulphonation is not advisable for all purposes, especially if the oil, for one reason or another, is used just as bought. If the above is true, it only tends to show the importance of this test. Mr. Schubert says that it is necessary to determine organically combined sulphuric acid

* Read at the 13th Annual Meeting, A. L. C. A., Atlantic City, June 2, 1916.

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($SO_3$) for factory control but that the user of the oil has no interest in it. Why not? It will be shown later that the analysis reported as he recommends to the committee may be practically worthless in valuing an oil, principally because of the omission of this test.

Our results show that the method for the determination of total sulphuric acid ($SO_3$) is accurate enough for practical purposes.

It may also be found by ashing 5 or 10 grams of the sample after the addition of sodium carbonate and then determining sulphates in the usual way. Following are some results by this procedure as compared with the provisional method:

| | Per cent. Total $SO_3$ | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Provisional Method | 2.30 | 2.04 | 3.02 | 5.24 | 5.12 |
| Adding Sodium Carbonate and Ashing | 2.34 | 2.14<br>2.05 | 3.14 | 5.43 | 5.25 |

The results by the latter method are a little higher and in view of what Mr. Oberfell says in reference to the provisional method, probably more accurate.

The methods for finding neutral oil are not very satisfactory, but we believe that sometimes useful information may be obtained. Oils of a given manufacture usually show a practically constant neutral oil figure if uniformly sulphonated and this determination may be of use as low sulphonation value may not be due to neutral oil present. For example—two oils, neither containing mineral oil, showed:

| | 1 | 2 |
|---|---|---|
| Neutral Oil | 46.50% | 10.50% |
| Combined $SO_3$ | 2.00 | 1.35 |

We have not found the determination of total fatty matter of much assistance in valuing an oil, although we do not undertake to say that such may not be the case. Some difficulty has been experienced in getting reliable, or uniform figures for oxidized fatty acids, our determinations varying considerably for the same oil. The total fatty matter in a highly sulphonated oil may appear lower than in one containing less combined $SO_3$ unless this figure is taken into consideration.

We are not in the position of the trades chemist whose customer will not pay for the analysis, but nevertheless have no desire to add to the time required or difficulties encountered in

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testing these oils. However, it seems to us that the following determinations are necessary, or at least useful:

Water
Ash
Ammonia
Neutral oil
Unsaponifiable oil
Organically combined $SO_3$
Inorganically combined $SO_3$.

The tabulations following show tests of six samples of oil. We give the tests practically as recommended by Dr. Bumcke, the Committee and also two individual members of the Committee.

TABLE:—NOTES ON SULPHONATED OIL ANALYSIS.

W. K. ALSOP AND L. A. CUTHBERT.

No. 1.

| | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | No. 6 |
|---|---|---|---|---|---|---|
| Moisture | 25.10 | 30.00 | 14.80 | 19.80 | 19.80 | 24.00 |
| Ash | 0.00 | 4.60 | 2.30 | 0.20 | 0.20 | 0.10 |
| Ammonia | 1.34 | 0.00 | 0.49 | 1.91 | 1.81 | 1.35 |
| Unsaponifiable | 0.50 | 14.60 | 0.80 | 1.60 | 2.10 | 9.80 |
| Neutral Oil | 8.80 | 6.20 | 46.50 | 7.60 | 10.50 | 12.00 |
| Total Fatty Matter | 64.80 | 49.60 | 80.70 | 73.90 | 76.60 | 56.30 |
| Oxidized Fatty Acids | 7.40 | 1.00 | 4.00 | 8.10 | 6.80 | 9.10 |
| Organically Combined $SO_3$ | 4.51 | 1.22 | 1.94 | 2.34 | 0.61 | 4.14 |
| Inorganically Combined $SO_3$ | 0.61 | 1.08 | 0.10 | 0.68 | 0.75 | 0.40 |
| Acid Value | 131.30 | 57.40 | 47.10 | 135.90 | 124.60 | 112.20 |

No. 2.—TESTS RECOMMENDED BY COMMITTEE.

| | | | | | | |
|---|---|---|---|---|---|---|
| Moisture | 25.10 | 30.00 | 14.80 | 19.80 | 19.80 | 24.00 |
| Ash | 0.00 | 4.60 | 2.30 | 0.20 | 0.20 | 0.10 |
| Ammonia | 1.34 | 0.00 | 0.49 | 1.91 | 1.81 | 1.35 |
| Unsaponifiable | 0.50 | 14.60 | 0.80 | 1.60 | 2.10 | 9.80 |
| Total Fatty Matter by difference 100% | 73.10 | 50.80 | 81.60 | 76.50 | 76.10 | 64.80 |

No. 3—TESTS RECOMMENDED BY SCHUBERT.

| | | | | | | |
|---|---|---|---|---|---|---|
| Moisture | 25.10 | 30.00 | 14.80 | 19.80 | 19.80 | 24.00 |
| Ash | 0.00 | 4.60 | 2.30 | 0.20 | 0.20 | 0.10 |
| Ammonia | 1.34 | 0.00 | 0.49 | 1.91 | 1.81 | 1.35 |
| Unsaponifiable | 0.50 | 14.60 | 0.80 | 1.60 | 2.10 | 9.80 |
| Neutral Oil | 8.80 | 6.20 | 46.50 | 7.60 | 10.50 | 12.00 |
| Sulphonated Oil by difference 100% | 64.30 | 44.60 | 35.10 | 68.90 | 65.60 | 52.70 |

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No. 4—Tests Recommended by Hoppenstedt.

| | | | | | | |
|---|---|---|---|---|---|---|
| Moisture | 25.10 | 30.00 | 14.80 | 19.80 | 19.80 | 24.00 |
| Ash | 00.00 | 4.60 | 2.30 | 00.20 | 00.20 | 00.10 |
| Total Fatty Matter | 64.80 | 49.60 | 80.70 | 73.90 | 76.60 | 56.30 |
| Unsaponifiable | 00.50 | 14.60 | 00.80 | 1.60 | 2.10 | 9.80 |
| Ammonia (Qualitative) | present | none | present | present | present | present |

We should class two of these oils as good, two as fair, one as poor and one as practically of no use as a sulphonated oil. We think a study of these tables will convince any of you that the tests in Tables 2, 3 and 4 give few data upon which to judge the value of some of these oils, also that the organically combined $SO_3$ (Table 1) throws considerable light upon the matter. It is not necessary to go into this in detail as it is sufficiently evident to those who may be interested. Emulsion tests are of course useful in testing these oils, but are difficult to describe, to carry out comparatively and we think, may sometimes be somewhat misleading.

DISCUSSION.

W. K. Alsop: In these tables you will note that the neutral oil varies from 46.5 per cent. to 6 per cent., and the organically combined sulphuric acid from 4.5 per cent. to 0.6 per cent. In the tests recommended by the Committee the oil would be valued by the fatty matter. In that case the poorest oil in the table shows up as one of the best. The tests recommended, in which the sulphonated oil is found by difference, show nothing about some of these samples.

E. J. Haley: This question of sulphonated oils is, in my opinion, a very important one, on account of the extensive and diversified usage, and speaking from a practical standpoint, I fully realize the weakness of the methods for the determination of the essential requisites of a sulphonated oil. Almost every laboratory has a different method, and what we should get after, if possible, is a standard method. We have here with us quite a number of experts on this sulphonated oil proposition, from the manufacturing, scientific and practical usage standpoints, and there is no time like the present to discuss it.

Dr. Gebhardt Bumcke: I was surprised when I saw in the Committee report that most of the members recommended to

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omit the test for $SO_3$. These oils are sulphonated oils, and they are called "sulphonated oils" for the simple reason that they are sulphonated. That means that the combination with the $SO_3$ group has changed the oil into an entirely different product. It should be the most interesting thing to determine the amount of $SO_3$ that has entered the oil.

There are other soluble oils in the market, many with fancy names, which generally are classified as ammonia oils, which look very much like sulphonated oils. They are made up by means of ammonia soap, and give a nice emulsion with water which looks very much like one made with sulphonated oil.

Accepting an analytical method as recommended by most members of the Committee, analysis made of these ammonia oils would not differ from that of the sulphonated oils. How shall we judge between them unless we determine the amount of $SO_3$?

I can tell you that, before the use of sulphonated oils became more general, I have been misled several times myself, when testing samples of soluble oils or emulsions and expecting to have before me an oil that probably was made with ammonia soap, or some other soap, I determined, as in the proposed method, water, fatty matter, unsaponifiable, ash and ammonia and eventually the free fatty acids; but trying to match the samples I saw that things would not work until I found that the sample in question was or contained sulphonated oil.

The same thing applied to another product that I had to match. I got it under a wrong name, and according to that did not suspect any sulphonated product. My experiments to match it, remained unsuccessful until again I found I had a partly sulphonated product before me. I therefore consider the tests for combined $SO_3$ an essential part of the analysis of the sulphonated oils or sulphonated oil products. I am very glad that in his paper Mr. Alsop brought up these details. The way I have represented the question of the $SO_3$ test in my article in the last November issue, is more or less from a scientific point of view, now we see its importance from the user's standpoint.

You see here, for instance, that the oil No. 1 has organically combined $SO_3$, 4.51 per cent. and oil No. 6, 4.14 per cent. They are certainly extremely good oils; while No. 3 and No. 4 might be classified as average oils, No. 2 with 1.22 per cent. $SO_3$ is

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rather poor, while No. 5 with 0.61 per cent. is very bad. The No. 1 and No. 2 may be mixed with other oils and carry those oils in solution, while if you tried the same thing with Nos. 2, 3 or 4, they would not work as well, while the No. 5 would hardly stand any addition of another oil and hold it in solution. You will find this out when you mix these oils with fatty or mineral oils. A good sulphonated oil that contains 3 to 4 per cent. combined $SO_3$ or more may be mixed with 50 per cent. or more mineral oil and would not separate, while everything lower in combined $SO_3$ will only carry less than that—maybe 30 or 20 per cent. This No. 5, I am sure, will not carry anything. The carrying power for other oils is certainly governed by the amount of combined $SO_3$ and for that reason, if for no other, we should not omit the determination of the $SO_3$ organically combined.

If, as recommended in my paper, we multiply this amount of combined $SO_3$ by 4.75—we obtain the percentage of sulpho fatty acids, and this figure certainly gives a good idea of the value of these oils. But I want to emphasize that this figure alone should never be taken to form the value of these oils, as the unsaponifiable and other items are very important too for a conclusion in regard to their value or usefulness. If you have an oil that is very well sulphonated, but containing a lot of unsaponifiable, you are not able to mix as much other oils with it as if it were pure, or in other words, the unsaponifiable according to its quantity depreciates not only the material value of the sulphonated oil, but also diminishes its carrying power for other oils.

Another factor is neutral oil. An oil though highly sulphonated might contain a lot of neutral oil which would decrease its carrying power for other oils, though its presence would not reduce its value in the same way as an equal amount of mineral oil. As usually in a tannery these sulphonated oils are mixed with other oils, it is an important factor that we look out for the ability of the oil to carry more. If you take an oil like this No. 1 and mix 30 or 40 per cent. mineral oil to it, you can get a clear solution in water, even with the mineral oil. It might be a little opaque, but you will get a nearly transparent solution. But if you tried the same thing with this No. 2, you would get an emulsion and the oil would probably soon separate.

Another important fact that I want to mention, is that the

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valuation of the oil should be based upon the purpose for which it is to be used. Many tanners use the oil as it comes, and that was the reason for complaints that we received that our oils were too highly sulphonated. These parties had been getting oils from another place which were lower in the percentage of combined $SO_3$ than ours; they mixed these with water and procured a splendid acid fat liquor. When they got our oil it would not work. Certainly not! On account of the higher amount of combined $SO_3$, it made a solution in water instead of a heavy, creamy emulsion; more oil, fatty or mineral, could have been added to it and it would have made a cheaper acid fat liquor than the product bought from the other firm.

In the Committee report there is a little mistake. On the second page (227) Mr. Oberfell says:

"The other appreciable error is due to glycerin and resolves itself into a question of which is preferred; total fatty oil as the original glyceride (found by Provisional Method) or total fatty acids (found by direct method). It is certain that when cod oil, neatsfoot oil, corn oil, etc. are bought, it is not on a basis of total fatty acids, but always in combination with the glycerin which constitutes the neutral oil. Consequently the Provisional Method gives results comparable to the original glyceride used in its manufacture." This is an error. The direct method does not determine total fatty acids, but total fatty matter, containing glycerides, free fatty acids, fatty acids from soaps, oxidized fatty acids and fatty acids from the sulpho-fatty acids having lost the $SO_3$ radical by the boiling with dilute HCl. On the other hand, the Provisional Method gives by no means the total fatty oil as the "original glycerides," but gives the total fatty matter with the same constituents just mentioned plus part of the sulpho-fatty acids (as the $SO_3$ of the sulpho-fatty acids will appear more or less in the ash according to how far the oil was neutralized with a fixed alkali.) In my article in the November issue I have called attention to other errors that lead to wrong results in the percentage of total fatty matter according to the Provisional Method; in my experience these errors amount to from 1 to 6 per cent., in the tests given by Mr. Alsop and Mr. Cuthbert they range from 0.5 to 8.5 per cent.

Now the glycerin that I meant is the free glycerin present in

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sulphonated oils to the amount of about ½ to 1½ per cent.; this is lost in the Provisional Method and calculated as fatty matter. Both methods find glycerides and free fatty acids. It is a misunderstanding that all fatty matter should be converted into fatty acids. When the oil is boiled with hydrochloric acid, the alkali is taken up by the hydrochloric acid and the group of $SO_3$ is separated from the sulpho-fatty acids and the total fatty matter thus found represents the fatty acids that were in the original oil, fatty acids that are separated from the sulpho-fatty acids, fatty acids formed during the sulphonation or washing process, and the original glycerides; the latter represent the neutral oil that is not in any way decomposed either by the sulphonation or by the boiling with diluted HCl.

On page 228 under "B"—No. 6, free fatty acids—I do not think that a determination of the free fatty acids is of any value, and especially not to the tanner. Mr. Alsop made a trial to determine the acid value of six oils and found results that varied from 47 to 135; they are evidently in no relation to the quality of the oils. I heard that he determined these figures by direct titration. Direct titration is impossible with sulphonated oils, or any product that contains ammonia. The titration does not stop as soon as all the free fatty acids are saturated, but it goes on, and the potassium or sodium takes the place of the ammonia, until all the ammonia soaps are converted into potash or soda soaps. The only way to determine free fatty acids in these oils is to determine the neutral oil and the total fatty matter, and subtract from the latter the neutral oil, the unsaponifiable and the sulpho-fatty acids minus combined $SO_3$—the rest would be free fatty acids.

C. R. OBERFELL: How about the ammonia soaps? How about the ammonia that has been added—ammonia soaps? You don't take account of that.

G. BUMCKE: I don't understand what you mean.

C. R. OBERFELL: It is possible to add ammonia to sulphonated oil and form ammonia soaps.

G. BUMCKE: You mean in the beginning?

C. R. OBERFELL: After you neutralize. Suppose you have carried it over the point of neutralization and you add an excess, it will unite with the free fatty acids, won't it?

G. BUMCKE: That is a question.

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C. R. OBERFELL: Why won't it?

G. BUMCKE: In making these oils you can see that when you have an oil that is very highly sulphonated it requires very little ammonia to neutralize this oil, a high amount of sulpho-fatty acids will clear up the oil with very little ammonia, while if the amount of sulpho-fatty acids is low you need more ammonia to clear that up, and probably you do not only neutralize the sulpho-fatty acids, but part of the fatty acids.

C. R. OBERFELL: That is the point I made; you neutralize the fatty acids and form an ammonia soap?

G. BUMCKE: Well, then you can figure that out—you have to determine the amount of ammonia and $Na_2O$ or $K_2O$.

C. R. OBERFELL: All right—if you take account of that, but you haven't taken account of it.

G. BUMCKE: You have to figure out how much of the alkali is needed for the $SO_3$ in salts, the rest first neutralizes the combined $SO_3$ (R—O—$SO_2$—OH) before any of the free fatty acids could combine with some alkali.

In reference to the importance of the $SO_3$ test I want to mention some experiments that I made some time ago, while we were making sulphonated oil in the factory; I took a sample, shortly before the washing in the factory was started, and washed and finished it in the laboratory, making up a product that contained the same amount of water as the product made in the factory. I tried to keep the conditions the same in the laboratory as in the factory, but they were still so different on account of the different quantities that the laboratory product showed 10 per cent. more neutral oil—that means unchanged oil—than did the product in the factory. The latter showed only 20, while mine showed 30 per cent.

But when I determined the combined $SO_3$ the laboratory product showed 3½ per cent., while the factory product only had 2½ per cent. This was all due to the different conditions of the washing processes. While local overheating may occur in a big bulk of oil, it would hardly take place in a small quantity. The product made in the laboratory was far superior to that made in the factory. A product showing 3½ per cent. $SO_3$ combined with fatty acids gives a very nice solution in water and carries a great deal more oil than a product that only contains 2½ per

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cent. You would imagine that an oil with 30 per cent. of unaltered oil in it, would not carry more other oil than one with 20 per cent. neutral oil, but the opposite was the case. The guiding factor is the $SO_3$ combined with fatty acids which enabled it to carry more than the other oil. What I want to show on these two oils is that the analysis of both according to the Provisional Method would be almost identical, perhaps show a little difference in the ash test, and yet these oils were widely different in quality and behavior.

I do not think that the ash test is of very great importance. If you want to determine how far an oil has been neutralized in such a case as Mr. Oberfell has just stated, it is necessary to determine the ammonia and the $Na_2O$. This ash test cannot help you to determine the free fatty acids. As I said before, the $SO_3$ is the most important figure, but that alone can never give us full information as to the value of the oil. I am glad that Mr. Alsop took up this matter, and I believe the best way to get an idea about the importance of the different figures of the analysis would be to determine on some oils that are used in the tannery, how the results from the factory agree with the figures we obtain in the laboratory.

E. A. PROSSER: I would like to ask Mr. Oberfell, in view of these analyses, which is the best of the five by the Committee's analysis.

C. R. OBERFELL: I don't know.

E. A. PROSSER: Which would you consider? You ought to have some opinion.

C. R. OBERFELL: I have absolutely no opinion on them. You will have to ask Mr. Alsop. He can tell you, because he knows. I have no opinion, because I do not use sulphonated oils except to a very limited extent.

J. H. YOCUM: Wouldn't the tests recommended by the Committee, with the addition of the organically combined $SO_3$ give you all the information it is desirable to have or is necessary? I mean to make a reasonable laboratory examination.

W. K. ALSOP: It would help a whole lot.

J. H. YOCUM: What other items would you consider essential to giving a fair idea of what the value of the oil was? Take your neutral oil and the organically combined $SO_3$—wouldn't the

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organically combined $SO_3$ added to the tests recommended by the Committee be all that you wish to have to make a judgment on these oils? Would the neutral oil make No. 3 better than No. 1?

W. K. ALSOP: No.

J. H. YOCUM: Then why have it? If you are going to base it on your organically combined $SO_3$, why have it?

W. K. ALSOP: It gives more information as to how the oil is made up.

J. H. YOCUM: Then you say that the combined $SO_3$ and neutral oil, added to the Committee's report, gives you everything?

W. K. ALSOP: It will give enough, everything that is usually necessary, and is practically what is recommended in the paper just read.

C. R. OBERFELL: While I was Chairman of this Committee, I do not consider that I am up on sulphonated oils at all, and if you will read this report carefully you will see that our work was based only on getting a unit for the buying and selling of oils. We did not do anything to determine the quality of the oils, and I am out for information on this point, the same as Mr. Mosser. Dr. Bumcke says an oil, highly sulphonated, will do in one place and won't do in another place, and I would like to have somebody tell me how you can tell that from the analytical data. There is no information you can get, except to take that oil and go out and experiment with it. You have got to buy it and use it before you can tell whether it is good or bad.

A. ROGERS: I think the first question a first-class tanner will ask the salesman, if he is going to use the oil for a fat liquor, is "How much other oil will it carry?" The point that Dr. Bumcke brought up is a very important one. I have used that to find out how much cod oil or neatsfoot can be added. In some cases you want to add cod oil, in another some degras, and sometimes you want to add neatsfoot, or possibly mineral oil. If you have an oil that is low in combined $SO_3$, it will not carry these other oils and when you make the fat liquor the oil will come to the top. This is a simple test to make and I think it is one that should be included. From my own experience, it is not so essential to know the actual fat liquoring power of the oil itself, as what you can use with it.

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E. J. HALEY: I would like to ask Dr. Bumcke a question or two. Assuming that you have two oils made from the same material—we will assume for the sake of argument that it is cod oil—will that oil showing the higher percentage of combined $SO_3$ show the lower percentage of neutral oil?

G. BUMCKE: No.

E. J. HALEY: Why not?

G. BUMCKE: The experiment that I just mentioned—the sample made in my laboratory shows it; the oils were sulphonated in the same way, and at a certain time both oils had that same amount of $SO_3$ in them that I found in the laboratory sample, but through the process in the factory that oil lost some again. This whole sulphonation process is not one that goes to a certain point and stops there; this is a process that always keeps on, so that if the oil is kept in contact with the sulphuric acid too long or under unfavorable conditions, the $SO_3$ group leaves again the fatty acid molecule and forms free fatty acid. In the product made in the factory the amount of neutral oil became 10 per cent. lower. You naturally come to the conclusion that if the oil contains less unaltered oil it would be higher sulphonated, but that is not the case. The product made in the laboratory was better, it kept the $SO_3$ group combined with fatty acids and in this way made a much better product even with 10 per cent. more neutral oil than the other.

Mr. Alsop has one oil on his list with 46 per cent. neutral oil, but the amount of $SO_3$ combined is almost 2 per cent., another oil has combined $SO_3$ 1.22 per cent. and only 6.20 per cent. neutral oil, while the No. 1 with 4.51 per cent. combined $SO_3$ shows 8.80 per cent. neutral oil. There is apparently no relation between the amount of combined $SO_3$ and the amount of neutral oil.

E. J. HALEY: It doesn't matter how much neutral oil you have in your product so long as you have a high percentage of $SO_3$?

G. BUMCKE: If you have two lots that show the same amount of $SO_3$ and one is 10 per cent. neutral oil and another 30 per cent., the one with the 10 per cent. seems preferable to me.

E. J. HALEY: And you consider the one with the higher percentage of neutral oil and the higher percentage of combined $SO_3$ the better product?

G. BUMCKE: You cannot do that.

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E. J. HALEY: What determines it? What is there in the oil that corresponds to the tannic acid in the extract as a standard of value?

G. BUMCKE: The ingredient of the oil that best indicates the value or degree of the sulphonation is the combined $SO_3$.

E. J. HALEY: Irrespective of any other property of the oil?

G. BUMCKE: Yes, irrespective of anything else. But then, if you have different oils to compare, there are other things to be considered—for instance, the amount of "$SO_3$ in salts," that indicates the amount of sulphates, sodium sulphate or ammonium sulphate in the oil. They are certainly not desirable, because if you have too much, your emulsion would not hold so well, say, in an oil that has 1 per cent. of $SO_3$ in salts as against another oil that has only 0.1 per cent. There is further the amount of water and of unsaponifiable that should be taken into account. So for instance, if you have two oils, one has 3½ per cent. combined $SO_3$ and 50 per cent. water, the other 3 per cent. combined $SO_3$ and 25 per cent. water; the first without question is more highly sulphonated, while with the second you get 25 per cent. more oil for your money. The first contains 7 parts combined $SO_3$ for every 100 parts dry oil, while the second only contains 4 parts combined $SO_3$ for the same amount dry oil. At the present high prices of all oils and greases the second oil surely will be more expensive, but the first may be used in certain combinations with other oils where the second oil might fail. Another time you may have an oil with 20 per cent. water, 20 per cent. mineral oil and 3½ per cent. combined $SO_3$, and another with 30 per cent. water, no mineral oil and 3 per cent. combined $SO_3$. The first product is more highly sulphonated, but contains mineral oil and if for a certain process in the tannery mineral oil is not wanted, the lower sulphonated product with no mineral oil will be preferable.

These examples show that the combined $SO_3$, though it may be the guiding factor, is not the standard value like tannic acid in extracts. There may be still other items, like the oxidized fatty acids, that may determine the value of the oil for tanning. The oxidized fatty acids in sulphonated cod oils seem to be identical with those in degras moellons; their amount varies from 5 to 15 per cent. according to my experience, and is, on the average, be-

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tween 10 and 12 per cent.; but of these we cannot say anything definite before the matter is further investigated.

C. EACHUS: I think the most important thing is the extent of neutralization. I think we should determine the amount of combined $SO_3$ in addition to the determinations Mr. Oberfell recommends and I believe this to be enough. But the extent to which a sulphonated oil is neutralized has more to do with its oil-carrying properties than anything else. I have seen sulphonated oils mixed with 75 per cent. of mineral oil to make a turbid solution, but if you neutralized it further and put more of the sulphonated fatty acids in it in the form of soap, 25 per cent. would combine with 75 per cent. of mineral oil and stay clear for 6 months.

I think in a properly sulphonated oil, the sulphonated fatty acids are in the form of sulphonated soaps, soluble in water, and the neutral oil and the free fatty acids can be separated by shaking up with sulphur ether and then evaporated down and weighed and determined in that way. If we determine the combined $SO_3$ and use that factor we can determine the sulphonated oil.

J. H. BARTON: I feel that if I say very much about sulphonated oils, I might be speaking too much from the salesman's point of view. In doing some work in the past year, I have been able to get a combination of heavy fats and sulphonated oil. This mixture was sulphonated, and would hold together in suspension with water, 10 per cent. solution, 80 per cent. of 28 gravity paraffine oil. When that combination was tried in a tannery against oils that had a high percentage of combined $SO_3$ and a low percentage of neutral oil, it would not give the result the tanner expected to get and compared very unfavorably with oils which had a high percentage of combined $SO_3$. So it appears to me, as far as I have gone, that possibly the combined $SO_3$ might tell you something, if you know how the tanner is going to use it. The manner in which he is going to use the oil will have a bearing on the value of the oil and as to what analysis to make. I do not think any set analysis would tell the tanner much as to what the oil is going to do for him.

C. EACHUS: I think our present analysis is sufficient to show how much water and unsaponifiable the tanner is buying and the combined $SO_3$ is chiefly qualitative to show it is sulphonated

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oil, but so far as it works in practice it depends on how the oil is neutralized and sulphonated and everything else.

E. J. HALEY: Then, with a theoretically sulphonated oil—100 per cent. sulphonated with no neutral oil present, what would you consider would be the percentage of $SO_3$ in the oil?

C. EACHUS: Well, I don't know. I never tried to figure that out. There would be free fatty acids there, too.

J. H. BARTON: I think that would be covered by the method of sulphonation; that is the method used in sulphonating your oils. I know of three or four methods and although you may get 100 per cent. sulphonation in one, that sulphonation would have no bearing on your combined $SO_3$, while in another method it would.

C. EACHUS: There is one method of sulphonation where they get about 50 per cent. of the free fatty acid separated from the oil. You can determine the neutral oil and the sulpho-fatty acids, subtract these from total fat to get free fatty acids.

J. H. YOCUM: Some two years ago, or it may be longer, a German chemist obtained a patent under which the sulphonation was carried on in the regular way, and the sulphonated oil then subjected to a comparatively high temperature. The $SO_3$ was driven off, and the resulting oil re-sulphonated. The claim made was that by this process 100 per cent. sulphonation could be effected with no fatty acids and practically no neutral oils.

In this connection this patent has a bearing on the subject under discussion. The degree of sulphonation is not entirely dependent upon the amount of combined $SO_3$; that is, when you once break the oil radicals down, it is an easy thing for two of the radicals to be attached to one $SO_3$ group, or in other words, the production of an oxysulphonated oil.

A MEMBER: I find that in a great number of oils. I find a variations of 8, 10 or 12 per cent., in oxidizing material present in the oil. We consider this due to overheating in sulphonation, so that two oils may have the same amount of sulphonation and still vary as much as 10 per cent. in the oxidizing material.

J. H. BARTON: I think some of the chemists have been misled somewhat. It appears they are assuming that manufacturers of sulphonated oils take in their original oil and sulphonate it in the condition in which they get it. If the manufacturers are refiners of oils, we have no proof that they have not treated their original

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oil to get these oxidized sulpho-fatty acids. I do not think it has been proven or can be proven that these oxidized sulpho-fatty acids came from the method of sulphonating.

G. BUMCKE: I did not think either that it came from the sulphonation. My investigations of that matter do not go far enough, but I have determined the amount of oxidized fatty acids in the original oil which varied from 3 to 5 per cent., and after the oil was sulphonated which showed then oxidized fatty acids from 9 to 12 per cent. I explain the thing in this way; in the washing process, by overheating locally, the molecule lost the $SO_3$ and then formed an oxy-product in the form of a lactone, or something like that, the elimination of the $SO_3$ group seems to be the cause of the forming of oxidized fatty acids.

We were discussing this subject in Mr. Oberfell's office, and I told him that on a number of oils I had determined the ozidized fatty acids because I thought it might be of some value. All sulphonated oils have a certain amount of oxidized fatty acids, and if we really knew these oxidized fatty acids do the trick, as those in degras and moellons, we should not only look for the amount of combined $SO_3$, but for the oxidized fatty acids as well.

T. J. MOSSER: One point that I don't quite understand the answer; and that is this, whether the amount of unaltered oil would affect the value considering that two oils had the same amount of combined $SO_3$; one having 20 per cent. of unaltered oil and the other 10 per cent., would the one with 10 per cent. carry more mineral oil than the one with 20 per cent?

G. BUMCKE: Yes, it would carry more than the one with 20 per cent.

T. J. MOSSER: In other words, the No. 1 oil, which contains 8 per cent. of unaltered oil and 4½ per cent. of $SO_3$ would be a better oil than the No. 6. That is, it would carry more mineral?

G. BUMCKE: Yes. It would carry more oil.

E. J. HALEY: The percentage of combined $SO_3$ depends largely on the process used in sulphonation. Is that not true, Mr. Barton?

J. H. BARTON: Yes, that is what I said.

T. J. MOSSER: Well, if he gets more in one way, that should carry more oil.

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E. J. HALEY: But the process may not permit of a higher percentage of combined $SO_3$. Is there any other thought to be brought out?

G. BUMCKE: The remark was made here that it would be interesting to know how far an oil is neutralized. You can see that when you pour about 2 cc. of the oil into a test-tube full of water. An oil that is neutralized to a certain point, but still acid, will dissolve very easily provided the oil is well sulphonated and has an amount of 3 or 4 per cent. of combined $SO_3$; it dissolves immediately making a thin emulsion or an opaque solution that becomes perfectly bright by the addition of a few drops of ammonia; an oil neutralized a little farther but still on the acid side makes a clear solution immediately; an oil just neutralized dissolves a little less easily, but will still do the same; but if it contains more alkali it forms little sausages or solid drops in the water and you have to shake more or less before they dissolve, to a usually cloudy solution. An excess of alkali acts peculiarly. You would think that if you had more alkali it would dissolve more easily, but the oil holds together and you have to shake it much more before it dissolves. This is a very sharp criterion for the degree of neutralization of these oils.

I have experimented on a good many and can find out immediately how far the oil is neutralized. No certain figure can be obtained by this test, but you can see from the behavior of the oil whether it is partly neutralized, wholly neutralized or has an excess of alkali.

J. H. BARTON: I would like to ask Dr. Bumcke whether he is speaking of one oil or different oils in general, that is, of one oil made by one process, or all oils in general?

G. BUMCKE: I am speaking here of oils of the same character. For instance, if you take castor oil; castor oil always runs higher in combined $SO_3$. You get a good product from cod oil with 3 or 4 per cent., while for castor oil it would not be considered a very good oil. Sulphonated castor oil often runs up to 5 or 6 per cent. combined $SO_3$. Comparing oils of the same character this neutralization test gives fairly good results except with oils that are low in combined $SO_3$ or contain much neutral or mineral oil. Such oils make an emulsion in water that would not brighten up to any degree by the addition of ammonia.

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## NOTE ON THE ACTION OF LIME IN THE UNHAIRING PROCESS*.

*By J. T. Wood, F. I. C., and D. J. Law, B. Sc., F. I. C.*

In a recent thesis presented to the University of Michigan by A. A. Schlichte on "The changes in skins during their conversion into leather."[1] the author shows that skins can be unhaired by sterile limes. His work was carried out in a very careful manner, and from his bacteriological results there seems to be no reason to doubt the conclusions arrived at. The editor of the JOURNAL of the American Leather Chemists' Association suggested to Mr. Schlichte that he might be in error as to the actual sterility of his lime liquors after the pieces of hide had been in for a considerable time, and several tests had been made on the condition of the hide by opening the vessels. Mr. Schlichte replied that the precautions taken were the same which he has used in very many experiments, and the proportion of contaminated cultures has been only one in 2,500. Further, in one experiment (No. 41) two flasks were charged, and left unopened for five months.

The editor appears to base his remarks on a paper by Mr. H. G. Bennett, published in the November issue of the same Journal, but we wish to point out that Mr. Bennett's conclusions still leave the question unsettled, although he says: "The hair is loosened almost entirely by the chemical action of enzymes which are supplied by the bacteria thriving in lime liquors. These enzymes dissolve the softer keratins and hair roots. This enzyme action is probably assisted to some extent by the chemical action of lime, not so much by its solvent effect, which is extremely small, as by its softening effect, which facilitates the enzyme action. If the keratinous matters yield any sulphur to the liquor, sulphydrate of lime will be formed, which will cause a very slight but direct chemical solvent effect."

The question was discussed in a paper by one of us in 1910,[2] in which it was pointed out that in ordinary working practice the main unhairing action in the limes is due to ammonia. The source of the ammonia was attributed to bacterial action, because

* *J. S. C. I.* May 31, 1916, pp. 585-6.

[1] Journal American Leather Chemists Assoc., 1916, p. 526, 585.

[2] *J. S. C. I.* 1910, p. 667, This J, 1910, pp. 360-83.

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the production of ammonia by the action of lime on skin in the cold appeared to be doubtful. Schlichte does not state whether his sterile limes which unhaired contained ammonia; this would be a most important point. In the same paper attention was also called to the fact, first stated by Payne, that calcium hydrosulphide, or sulphydrate, is produced by the action of caustic lime on the sulphur in the hair, and that this has an unhairing action.

The present note is to give the results of a hitherto unpublished experiment carried out by the authors in 1910, which appears to throw some light on Mr. Schlichte's results.

Although it is difficult to sterilize skin effectively without altering it to some extent, it is comparatively easy to sterilize hair and lime water. The experiment was made to determine the action of lime water on calf hair. Two bottles were prepared containing a few grams of pure lime, and 200 cc. of water. One of these was sterilized by steaming in the usual way, and then partly filled with clean calf hair, which had been sterilized by boiling. The other bottle contained calf hair in lime water without any sterilization. The bottles were sealed antiseptically, and put away in a dark cupboard. The hair was observed to be gradually attacked in both bottles. After an interval of 114 days, the hair had almost completely disappeared in both bottles, whilst the liquid above was of a yellow color. That in the unsterilized bottle gave off ammonia on boiling; 25 cc. distilled into 25 cc. N/10 acid required 20.7 cc. N/10 soda for neutralization, *i. e.*, the ammonia was equivalent to 4.05 cc. N/10 acid, or 0.00567 gram nitrogen, equivalent to 0.227 gram per liter nitrogen in solution. The liquid on acidifying and boiling gave off $H_2S$, and a precipitate was formed (sulphur?). The soluble sulphur was estimated by oxidation with bromine water, and precipitating with barium chloride; 15 cc. gave 0.031 gram barium sulphate, equivalent to 0.00426 gram sulphur, or 0.284 gram sulphur per liter.

On opening the sterile bottle inoculations were made into nutrient gelatine tubes. These showed no growth after one week at room temperature, so that the solution was sterile. The clear supernatant liquid was analyzed in the same way as that in the unsterilized bottle. Ammonia was present; 25 cc. of the liquid distilled into 25 cc. N/10 acid required 21.6 cc. N/10 soda for neutralization, so that ammonia equivalent to 3.4 cc. N/10 acid,

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or 0.2312 gram ammonia per liter, or 0.1904 gram nitrogen per liter was present. On acidifying and boiling $H_2S$ was given off: 20 cc. after oxidation with bromine as before yielded 0.0194 gram barium sulphate, equivalent to 0.002664 gram sulphur, or 0.13332 gram sulphur per liter. The results are shown in the table, grams per liter:

| | Unsterilized | Sterilized |
|---|---|---|
| Nitrogen in solution | 0.227 | 0.1904 |
| Sulphur | 0.284 | 0.1332 |

The sulphur in the unsterilized bottle was equivalent to 2.13 grams per liter $Na_2S + 9H_2O$. That in the sterile bottle was equivalent to 1 gram per liter.

Schlichte found that in sterile limes the hair could be removed with difficulty after 11 days, but after 13 days it could be removed easily.

In order to ascertain whether a sterile solution containing an equivalent amount of sulphur in the form of sodium sulphide would unhair sterile skin, calf skin was sterilized by the Seymour-Jones process. The sterilizing solution was made up of 5.5 cc. 90 per cent. formic acid, and 0.2 gram mercuric chloride, the skin being left in this solution for 24 hours. The skin was found to be quite sterile by bacteriological tests. It was then placed in a sterile solution, consisting of excess of lime, and 1 gram of crystallized sodium sulphide. The skin when put into this solution turned a pale green color, and retained its swollen condition in the lime, although the acid was, of course, neutralized. In 44 hours the hair could be removed with some difficulty, but after a further 12 hours it slipped easily. The solution and the skin were both sterile to bacteriological tests. It is thus shown that 1 gram per liter of sodium sulphide in the presence of lime will unhair skin in a sterile solution.

The action of lime on hair in the cold is slow, but it is greatly accelerated by heat. Calf hair boiled for one hour with lime water, and afterwards kept at 37° C. for 12 hours, contained (0.255 gram per liter) sulphur; depilation was complete in 48 hours in this solution.

With regard to the influence of time on the action, a flask containing sterile lime and sterile calf hair, after standing for eleven days at room temperature, was found to contain 0.077 gram sul-

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phur per liter. This is not so much as that found in the original experiment above cited, but was found to be sufficient to loosen the hair.

In the experiment cited it will be noted that more sulphur is dissolved under non-sterile conditions than under sterile conditions, although it is possible that some sulphur was lost in sterilizing the hair, as a portion of the sulphur is very loosely held. The experiment, however, supports the conclusions reached by one of us (this J., 1910, 668), namely, that if sufficient time be given, a sterile lime will unhair skin.

To sum up, the unhairing action of lime water in practice appears to be due to several causes:

1. Ammonia, produced generally by bacterial action in the old limes, but also by the chemical action of lime on the hair and certain constituents of the skin.

2. Weak proteolytic enzymes produced by bacteria.

3. Sulphur compounds formed by the action of lime on the easily dissolved sulphur in the hair.

Each of these actions will cause depilation, and in practice all three are present. In Schlichte's experiment, No. 3 is the probable cause of the depilation.

It is possible that the swelling of the skin in the sterilizing solution, and the subsequent neutralization by the lime, may have some effect in the unhairing. In this case, the part played by the sulphur would not be essential, but merely an accompanying effect. This point is being further investigated.

Since Mr. Law joined H. M. forces, I have had considerable assistance in the analytical work from Mr. A. Baumfield, to whom our thanks are due.

## Discussion.

Mr. J. M. Wilkie observed that the concentration of soluble sulphur, which was initially zero, rose as the action progressed. so that an explanation was still required as to the mode of action of the sodium sulphide produced.

Mr. Dunford asked whether sulphur disintegrated or dissolved the hair as well as keratin.

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Dr. Prideaux asked whether ammonia and sodium sulphide had the same dehairing influence.

Mr. Pentecost expressed surprise to hear that sodium sulphide did not injure the skins, because in the case of animal products such as silk sodium sulphide was very injurious; it took away that loose, pleasant feel. Lime acted in the same way, but it was more energetic than sulphide.

Mr. Innes said that the function of the liming process was not only to unhair. In their own experiments they had been led to suspect a certain amount of putrefaction. The action of lime might be hydrolytic or it might be a purely solvent action. An excessive liming would destroy the fiber and possibly the same thing could happen with keratin.

Mr. Duncalfe said that the horn part of animals consisted of keratin, growing in close contact with the horn pith in the same way as hair on skin; it was very difficult to remove the horn from the pith in the ordinary way, the general process being to keep the horns for a very long time in the open air; that process, he concluded, was due to bacterial action, probably producing ammonia. If horns were allowed to get hot the horns would come away very much more quickly, probably owing to the bacterial action being very much more rapid. The bacterial action in that process was very great, judging from the liquid that came away.

Mr. Wood said that in ordinary practice the bacterial action was very prominent in all those cases. The prevalent idea was that this was really the cause, as it had been stated by several authors that sterile liquors would not unhair. Probably the action Mr. Duncalfe mentioned was very much the same as took place if a skin were left lying about: the hair would become loose and could be pulled out. With regard to the elimination of putrefaction, there were difficulties in the way of using disinfecting materials in the soak. It was usual to use some coal tar product like phenol, but formaldehyde was fatal. It was impossible to make glue of the pieces afterwards. It had been found by Stiasny that each alkali had a different action. The swelling action depended on the hydroxyl-ion concentration but not the unhairing action. Keratin did not swell; it simply softened. Sulphide dissolved it absolutely, hair root as well, but ammonia

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just dissolved the layer round the root of the hair. That question of hydroxyl-ion concentration had been gone into very thoroughly, and it had been found that the order of swelling was the opposite to that of unhairing. Silk was not keratin, but was allied to keratin. Hair contained about 80 per cent. keratin; horn probably the same. In practice the unhairing action was always due to bacteria when they were present in quantity; bacterial action alone was sufficient to unhair. Sulphide unhaired by dissolving the hair, whereas bacteria only attacked the hair roots. That was why the old system of sweating (hanging the skin in a cool place) was still used, because the wool was not damaged and was more lustrous than if removed by any other method.

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## THE LAWS AND REGULATIONS AS AFFECTING THE IMPORTATION OF CATTLE, SHEEP, AND GOATS, AND THE HIDES, SKINS, AND ALLIED PRODUCTS OF THESE ANIMALS.*

*R. W. Hickman, Ph. G., V. M. D.,*

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With a view to the prevention of the introduction of diseases of cattle into the United States, the first session of the 39th Congress, under date of December 18, 1865, passed the first act providing for the prohibition of the importation of cattle from foreign countries. The same Congress, under date of March 6, 1866, amended this act, making it apply likewise to the hides of neat cattle. The Secretary of the Treasury was directed to make such regulations as necessary to put the law into immediate effect. This same law was reenacted in 1874 as a part of the Revised Statutes.

The first prohibition under the act was issued by the Secretary of the Treasury on July 31, 1875, excluding cattle and the hides of neat cattle from Spain on account of the presence of foot and mouth disease. This order was withdrawn in October of the same year, and on November 3, 1875, a similar order was made

* Address at the meeting of the National Association of Tanners, New York, June 1. *S. and L. Rep.*, June 8.

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prohibiting the importation of neat cattle and the hides of neat cattle from Great Britain and Ireland on account of the prevalence of foot and mouth disease. This order remained in effect until March 16, 1876, when the Secretary of the Treasury allowed the importation of blooded stock from Great Britain and Ireland, provided they were accompanied by a certificate from the United States consular officer that such animals were at the date of exportation in a sound and healthy condition and free from foot and mouth disease or any indication thereof. On February 26, 1879, as the Treasury Department learned that contagious pleuropneumonia existed in England, the ports along the Atlantic seaboard were closed to English cattle until otherwise ordered. This prohibition against England was revoked July 1, 1879, and suspended as to European ports, provided all cattle should be kept in quarantine not less than 90 days under Customs Officers at the expense of the parties interested.

The discovery that contagious pleuropneumonia existed among American cattle and the order issued by the Privy Council of Great Britain in 1878, requiring the slaughter of American cattle at the port of landing, led to the appointment of the Treasury Cattle Commission, consisting of Prof. James Law, J. H. Saunders, and Dr. E. F. Thayer.

On July 30, 1883, the Secretary of the Treasury issued an order requiring that all neat cattle from any part of the world, except North and South America, be subjected to a quarantine of 90 days at the port of entry. Stations for the accommodation of imported cattle were provided at the ports of Portland, Me., Boston, Mass., New York, N. Y., and Baltimore, Md.

By a provision of the Sundry Civil Bill approved July 7, 1884, money appropriated for establishing and maintaining quarantine stations for neat cattle was to be expended by the Commissioner of Agriculture under the supervision of the Secretary of the Treasury, accordingly on August 25, 1884, the Commissioner of Agriculture issued an order specifying that all neat cattle arriving in the United States from any part of the world except North and South America be landed only at such ports along the Atlantic seaboard as were provided with cattle quarantine accommodations under control of officers of the Department of Agriculture

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and that persons contemplating the importation of cattle must obtain permits. This law applied to only one class live stock, namely neat cattle. On account of the danger of importing disease in other classes of animals, the Act of August 30, 1890 was passed, including sheep, other ruminants and swine, with neat cattle and prohibiting the importation of any such animals as were diseased or affected with any disease or which had been exposed to such infection within sixty days next before their exportation. The administration of this law was entrusted to the Secretary of Agriculture, who was authorized to retain in quarantine all neat cattle, sheep, other ruminants, and swine imported into the United States at such ports as he should designate. The regulations now in force for the inspection and quarantine of cattle, sheep, other ruminants, and swine imported into the United States are made under authority of this Act (approved August 30, 1890) supplemented by later acts.

Animal quarantine stations have been continuously maintained at the ports of Boston, New York and Baltimore since authorized by Congress in 1883.

There have been various reenactments of the law giving the Secretary of the Treasury authority to control the importation of neat cattle and the hides of neat cattle, the last of which is designated as Section IV-H, subsection 1, of the tariff act of October 3, 1913, and is a reenactment of the act of 1909 authorizing the Secretary of the Treasury to suspend the prohibition as to any foreign country or any parts of such country or countries, whenever he shall officially determine, and give public notice, etc.

Subsection 2 of this act provides as follows:

"That any person convicted of a wilful violation of any of the provisions of the preceding subsection shall be fined not exceeding $500, or imprisoned not exceeding one year, or both, in the discretion of the court."

Under the old Act of April 23, 1897, the President of the United States was authorized to suspend the prohibition against neat cattle and the hides of neat cattle whenever the Secretary of Agriculture should certify to him what countries or parts of countries were free from contagious or infectious diseases of domestic animals, in order that neat cattle, domestic animals, and

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hides might be imported from such countries without danger to the domestic animals of the United States.

The Congress later conferred this authority upon the Secretary of the Treasury and provided that he should officially determine and give public notice thereof when such importation would not tend to the introduction or spread of contagious or infectious diseases among the cattle of the United States. Accordingly, the regulations governing the importation of hides of neat cattle have been issued by the Secretary of the Treasury, and while the regulations governing the importation of cattle, sheep, other ruminants and swine are issued by the Secretary of Agriculture, the Secretary of the Treasury, under the authority of law now in effect, as indicated in the Tariff Act of October 3, 1913, must officially determine and give public notice thereof whenever the prohibition against the importation of cattle is suspended as applying to any foreign country or countries or any parts of such country or countries. Countries from which cattle can now be imported by such suspension of the operation of the law are Great Britain, Ireland, the Channel Islands, New Zealand and North America. In case importations of cattle from other countries were contemplated, it would be necessary for the Secretary of the Treasury to officially determine and give public notice thereof in order to comply with the requirements of the law.

Prior to the organization of the Bureau of Animal Industry in 1884, the sanitary control of both cattle and hides was under the Treasury Department. That Department has continued to issue the hide importation regulations and the Department of Agriculture the regulations governing the importation of live stock, the supervision of both being directly under the Quarantine Division of the Bureau of Animal Industry and this work includes the supervision of importations and exportations of live stock, the importation of hides, skins, glue stock, hair, wool, and allied animal products, hay, straw forage, and similar materials, and the administration of the regulations in connection therewith, the authority for which is contained in Section 2 of the Act of February 2, 1903, which reads in part as follows: That the Secretary of Agriculture shall have authority to make such regulations and take such measures as he may deem proper to prevent

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the introduction or dissemination of the contagion of any contagious, infectious, or communicable disease of animals from a foreign country into the United States . . . and to seize, quarantine, and dispose of any hay, straw, forage, or similar material, or any meats, hides, or other animal products coming from an infected foreign country to the United States.

It is probable that when new regulations are issued they will be issued jointly by the Secretary of the Treasury and the Secretary of Agriculture and be made to include all of the various products named in the above mentioned Act.

The regulations now in effect which are the latest issued by the Secretary of the Treasury governing the importation of hides, are known as Treasury Department Circular No. 23 (Division of Customs) of May 2, 1910. This, as amended, provides that abattoir hides the product of Sweden, Norway, New Zealand, Australia, Great Britain and Argentina may be imported without disinfection when accompanied by a certificate of an official veterinarian of the country where slaughtered showing that the same were taken from cattle free from disease at the time of slaughter, and that all other hides of neat cattle, including calf skins, from any part of the world except North America, must either be accompanied by a certificate signed by the American Consul of the district from whence shipped, stating that anthrax is not prevalent and that neither foot and mouth disease nor rinderpest exists in such district, or they must be accompanied by a certificate signed by the American Consul showing disinfection by immersion for 30 minutes in a 1 to 1,000 bichloride of mercury solution. If certified by the American Consul as coming from a district in which anthrax is not prevalent (but in which foot and mouth disease or rinderpest exists), a certificate of disinfection by immersion in a 5 per cent. solution of carbolic acid will be accepted. In the case, however, of hides from districts in which anthrax is prevalent, disinfection by immersion for at least 30 minutes in a 1 to 1,000 solution of bichloride of mercury only will be permitted.

Treasury Department Circular No. 23, of May 2, 1910, provides further that hides of a character requiring disinfection, which are not accompanied by a proper certificate of disinfection will be treated as prohibited importations and refused entry, and

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that disinfection by immersion for at least 30 minutes in a 1 to 1,000 solution of bichloride of mercury will be required for all hides of neat cattle, as well as hide cuttings and parings, or glue stock, imported from any country, when shipped from districts in which anthrax is known to the consul to be prevalent at the time of shipment. The circular also provides that disinfection of such hides on the dock of the importing vessel upon arrival in this country, or their entry for transportation to another country across American territory, will not be permitted.

Attention is invited to the precautionary measures in force governing the importation of the live animals.

It is the policy of the Department not to permit the importation of cattle, sheep, other ruminants and swine from any country in which foot and mouth disease, rinderpest, pleuropneumonia, or surra is present. The regulations as applying to hides make restrictions against the two diseases first named and anthrax. To safeguard against the importation of anthrax infection in live stock, the regulations known as B. A. I. Order 209, require that any person contemplating the importation of cattle, sheep, other ruminants, and swine must first procure from the Secretary of Agriculture two permits. The permits are issued in triplicate, two to go to the importer, one copy of which is delivered to the American Consul at the port of shipment, one accompanies the shipment to the Collector of Customs at the port of entry and the third is held by the superintendent of the animal quarantine station at the port of entry.

These regulations provide that all such animals shall also be accompanied by a certificate from the local authority of the district in which the animals have been continuously located during the preceding six months, stating that no contagious pleuropneumonia, foot and mouth disease, anthrax, rinderpest, or any other disease contagious to cattle (except tuberculosis) has existed in such district.

They also provide for affidavits of the owner, importer or his agent, and the shipper, to show that no contagious disease affecting the species of animals has existed among them nor among any animals of their kind with which they have come in contact for six months last past and that they have not passed through any

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district in course of shipment infected with contagious diseases affecting the same kind of animals. These certificates and affidavits must be presented to the Collector of Customs at the port of entry when the animals arrive and be delivered by him to the inspector of the Bureau of Animal Industry stationed at such port in order that the animals be landed subject to his inspection and admitted to quarantine. Cattle from Great Britain, Ireland and the Channel Islands are held for a period of 30 days. Those imported from other countries (except North America) are subject to a quarantine of 90 days. Thus the Department has a complete check on importations of live stock and by these regulations diseases from abroad through such importations have been excluded.

While this may appear to have no particular bearing upon the regulations governing the importation of hides, I thought it would be interesting to you to know the precautionary measures which are considered necessary to prevent the introduction of disease from abroad through the live animals. It is believed, however, that it can be said without any mental reservation whatever, that the most difficult problem with which the Bureau of Animal Industry has to deal is that pertaining to the formulation and administration of efficient sanitary measures and regulations for the importations of hides, skins and allied animal products. It appears that practically all countries of the world having such products to export and seeking a market in the United States are more or less overrun by one or more of the dreaded animal plagues and are either without any sanitary organization whatever or without adequate sanitary requirement to prevent the shipment of the infection of the disease scheduled in the hide regulations.

Recently a modification has been made in the disinfection requirements by permitting under proper safeguards the forwarding of hides unaccompanied by certificates as required by the regulations, for disinfection at the tannery or point of destination in this country if provided with facilities for such disinfection. Hides which arrive without certificates of any kind are permitted transfer to the tannery in cars under customs seals after being thoroughly sprayed with whitewash under the supervision of the

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inspector in charge at the port of entry and disinfected in a 1 to 1,000 solution of bichloride of mercury with 48 hours exposure. If the hides are accompanied by a consular certificate showing the non-prevalence of anthrax, disinfection at the tannery is permitted in a 1 to 5,000 solution of bichloride of mercury or a five per cent. solution of carbolic acid with not less than 24 hours exposure, as the milder form of disinfection is considered to be effective in the sterilization of the hides for possible foot and mouth disease and rinderpest infection.

It is the aim of the Department to institute only such sanitary measures in connection with the importation of hides, skins and the other animal products as are considered necessary in safeguarding this country against the introduction of animal diseases from abroad and to accomplish this with the least possible inconvenience, hindrance or detriment to the tanning and associated industries. In an undertaking of this character, like all others involving numerous and varied interests, co-operation is the keynote to success and upon this basis depends the satisfactory accomplishment of our mutual purposes, *i. e.*, the procuring in this country of these products from abroad and the exclusion at the same time of disease from foreign countries through such products. It will have been observed that these laws and regulations are administered and the work of carrying out their requirements is accomplished through departmental co-operation. The consular service belongs to the Department of State, the Customs Service to the Treasury Department, and the Bureau of Animal Industry to the Department of Agriculture. But for the satisfactory accomplishment of the ends in view your hearty co-operation is just as important and it is gratifying to say that a fine spirit of co-operation on the part of some of your members has been manifested and it is believed that our conferences and meeting together will be conducive to a better understanding and a more general co-operative spirit and purpose.

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## ABSTRACTS.

**The Utilization of Water Sulphite Lyes.** JAMES BEVERIDGE. *J. S. C. I.*, May 31, 1916, pp. 563-5. Dry spruce wood, which forms the principal raw fibrous material for the manufacture of cellulose in Canada, contains 53 per cent. cellulose, 29 per cent. lignin, 14 per cent. other carbohydrates, 3.3 per cent. resin and 0.7 per cent. protein. The two systems of cellulose manufacture are the Mitscherlich "slow-cook" system and the Ritter-Kellner "quick-cook" system. In the former the temperature does not exceed 120° C. In the other, the cooking is done much more quickly at temperatures up to 155° C., the fiber being less strong than that produced by the first process. The effect of this difference of temperature on the products other than cellulose has not been investigated. The waste lye from the Mitscherlich system is generally clear and of a bright yellow color and contains from 0.47 to 1.56 per cent. sugars, while that from the Ritter-Kellner system is usually turbid and dark brown, containing from 0.89 to 2.02 per cent. sugars. The sugars are of great importance, as they form the basis of the manufacture of ethyl alcohol from these lyes.

An analysis by Winchelhaus of the waste lye from spruce treated with bisulphite of lime is as follows: dry residue, 8.28 per cent. (organic, 6.83 per cent.; inorganic, 14.45 per cent.); $SO_3$, 0.34 per cent.; combined $SO_2$, 0.58 per cent.; free $SO_2$, 0.26 per cent.; Cl, 0.0024 per cent.; $SiO_2$, 0.00024 per cent.; $Fe_2O_3$ and $Al_2O_3$, 0.001 per cent.; CaO, 0.72 per cent.; MgO, 0.0004 per cent.; alkalies, 0.002 per cent.; specific gravity, 1.039. Practically all the lime is combined either with the sulphuric acid or with the organic matter. Of the organic compounds, the most important are those which form insoluble compounds with gelatine or hide, and can therefore be used in leather manufacture, and the sugars, which may be converted into alcohol.

The following are suggestions for the disposal of the lye, without subjecting it to any chemical treatment except the neutralization of the free $SO_2$. (1) Laying the dust on roads. (2) As a cementing material in the manufacture of briquettes from sawdust and coal dust. (3) In the preservation of timber, mixed with other materials, such as zinc chloride. (4) As an artificial manure, mixed with fine-ground slag. (5) As a source of wood-pitch, when evaporated to a high density and dried on a steam drum. (6) As a binding material for the sand in foundries, and (7) as a mordant in dyeing certain textile fabrics. Efforts have been made to utilize it as a sizing material for jute and other coarse fabrics, but the odor is objectionable, and it is hygroscopic. Exposure to moist air causes decomposition with the evolution of hydrogen sulphide.

Two methods of regenerating the lye for re-use have been devised. By nitration, a yellow dye has been prepared, which is said to be light-fast. Any process, to be satisfactory, must provide for the disposal of all the lye. The outstanding features of the problem are the recovery of the pseudo-tannins and fermentable sugars, and the recovery for re-use of the sulphur and the base, particularly when this base is soda.

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When the lye is neutralized with lime, and the clear liquor evaporated down, it may be sold as a tanning agent, and is extensively used in conjunction with quebracho, hemlock, valonia, etc., in the manufacture of leather. Notwithstanding the prejudice against it, its use appears to be increasing. The separation of the pseudo-tannins from the fermentable sugars is a problem of the greatest importance which remains unsolved. The names of Wallin and Eckström are connected with the origin and development of the process for converting the fermentable sugars into alcohol. The hot lyes are freed from $SO_2$ by boiling *in vacuo* or by the addition of lime, the recovered $SO_2$ or calcium sulphite is sent back to the sulphite plant for use. The lyes are then cooled, and the last traces of acid removed, preferably by means of ammonia. The prepared lyes are now fermented by means of a special yeast and the alcohol distilled off.

The recovery of the base, when this is soda, is not difficult. It may be done by the Leblanc process. The cooking operation is carried out with greater ease when soda is used, and the pulp obtained is of better quality than that produced with lime or magnesia bisulphite. Several other methods for the recovery of soda and sulphur are described.

**New Tanning Bark.** *Hide and Leather*, May 27. An Australian correspondent of the *Leather Trades Review*, London, says a new tanning bark has recently arrived on the home market from New Zealand under the name of Tanekehi bark; this bark gives a liquor of reddish cast, which, of course, is rather objectionable, but contains a fairly high percentage of tannin, *viz.*, about 28 per cent. We understand there is an idea, on the spot, of making a liquid extract from this wood; as it should be practicable to minimize the reds in the process, this should, if successful, give a welcome addition to our limited stocks of tanning materials.

**Tanning Materials Scarce.** *Hide and Leather*, May 27. The Liverpool, Warrington and district branch of *The Shoe and Leather Record*, London, England, says American extract is reaching that country in driblets, and the total quantity is not sufficient to keep the trade going. No news of the French extract is to hand; indeed, one or two tanners complained of the way they are kept in the dark on these matters by the committee of the Federation.

**Canadian Laboratory.** *Hide and Leather*, May 27. Yocum-Faust, Ltd., has been incorporated as analytical and manufacturing chemists, and to conduct a laboratory for the Canadian leather trade, in London, Ontario. This concern is a branch of the John Yocum Laboratory, Newark, N. J., and is also manufacturing sulphonated oils for the tanning industry. The business is under the personal supervision of Thomas A. Faust, a well-known and popular leather chemist, formerly in the Yocum Laboratory at Newark.

**Tanning School and Research Laboratory.** *S. and L. Rep.*, June 8, 1916. At the semi-annual meeting of the National Association of Tanners,

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New York, June 1, 1916, President H. F. Lesh referred in his report to the establishment of the new eastern office of the Association at Boston, to the British embargo on hides and skins, to the Federal Trade Commission, to the anthrax disinfection regulations, the Chicago strike, and the recent shoe and leather conference in Philadelphia. George H. Raymond spoke on the work of the Tanning School at Pratt Institute, and made the following remarks about the Tanning School and the Research Laboratory:

"Five years ago this work was started under the supervision of this Association. As to the value of this work, and the advantage of this technical training, there are members of this Association who can testify, having had some of the graduates of the Tanning School in their employ.

"At the annual meeting of 1914 an Advisory Committee was appointed, consisting of three tanners and three members of the Association of Leather Chemists, and this Committee has so far remained unchanged, and has been the means of bringing the Association in closer touch with the Tanning School.

"At the annual meeting of our Association, held in Chicago last October, it was unanimously decided to make a further advance, and in line with the scientific preparedness of the day, establish a Research Laboratory. This to be effective must have at its head a chemist of marked ability and the minimum of cost to carry on the work both of the Tanning School and the Research Laboratory was estimated to be $15,000 a year.

"The matter of raising this fund was left with the Finance Committee, and an appeal has been sent out by the President asking if the party receiving it would be one of fifty to guarantee for five years their proportion of this amount. I learn from our Executive Secretary, Cudworth Beye, that sixty-two members have expressed their willingness to subscribe toward the $15,000 a year subscription fund. Eighteen of these subscriptions are based on $300 a year for five years, and of these eighteen, fourteen are willing to aid in underwriting the fund.

"We earnestly desire and appeal to all members of the Association to take such part in this subscription as they may feel justified in doing, as the work of the Tanning School is a matter which relates to the entire trade including all groups and all varieties of leather. It is hoped that some of the men of means in our trade, men of broad vision, will take this matter under thoughtful consideration, and either by direct endowment or by legacies, create an endowment fund, from which a permanent income can be derived.

"Yesterday at the meeting of the Advisory Committee at the Pratt Institute in Brooklyn, we had the pleasure of having a number of gentlemen with us, an invitation to the entire Association having been extended, so that the members of the Association might have an opportunity to inspect for themselves, the Tanning School, in the new quarters of the Institute to which it has been moved, and with its larger and better facilities and equipment, and see how the work is conducted, also to meet

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with the Committee, and express their views, or give their suggestions as to the matters in which they were personally interested.

"Last year of the twenty-one graduates, all secured positions, and of the twenty-four taking the course this year, nineteen tanners and five in applied leather chemistry, we learn that all but two have positions in prospect. Most of the students have had some experience in tanneries.

"It may be well to call to your attention the fact that none of the amount appropriated by the tanners' fund is paid toward the salaries of the professors, or expenses of the Institute, and I understand that last year the Pratt Institute contributed an amount of about $6,000 of the income of their endowment fund in excess of the tuition fees.

"The tanners have awarded this year, and the same has been recommended for the coming year, four scholarships to the students at $300 each, and one scholarship to the leather chemists of $400. These are given to young men of limited means, who show a marked interest in the work they have in hand.

"The students are taken during the year on observation trips to different tanneries, and doubtless some of the gentlemen present have had an opportunity to entertain them and show them through their plants.

"There are some lectures provided for the tanners outside of the regular course of instruction, and also a certain amount for special investigations, and for printing, reports, etc. The entire amount heretofore appropriated for the last five years averaged less than $5,000 a year.

"The Association having laid a broad foundation for the tanning school, it remains for them to develop and build up the school; and from the experience of the men who have studied in the schools abroad, we see no reason why a tanning school in the United States should not in time take the foremost rank, and such is the aim, ambition and ideal which your Committee have set before them."

## PATENTS.

**Process for Drying Artificial Leather. U. S. Patent 1,186,052.** R. WEEBER BÄRN, Austria-Hungary.

**Method of Treating Hides. British Patent 1,375.** W. OWEN, Warrington, England. The hides are treated with pure sodium chloride, sodium carbonate and tannic acid, before being unhaired or fleshed.

**Leather Substitutes. British Patent 2,633** (patent suspended). E. WAGNER, Berlin.

**Treating Sewage. British Patent 1,141.** W. JONES, Stourbridge, England. Air is passed through sewage in the process of treatment with activated sludge, at varying rates, so as to promote bacterial growth.

**Tanning Substance. U. S. Patent 1,186,500.** A. RÖHMER, Stuttgart, Germany, assignor to the German Colonial Tanning and Dyestuff Materials Company. Formaldehyde and an oxynaphthalene compound are the materials used.

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**Flexible Roll for Leather-splitting Machine. U. S. Patent 1,186,123.** C. OPPENHEIMER, Strassburg, Germany.

**Leather Seasoning Machine. U. S. Patent 1,186,126.** W. E. AND J. P. POINSETT, Wilmington, Del.

**A New Tanning Process,** which has been patented in France by M. J. Boilley, consists essentially in subjecting the skins to the preliminary action of a special mordant, with the object of fixing the tanning substances in the fibers of the skins more rapidly and permanently. The process can be applied either to the so-called "rapid tanning" or to slow tanning—that is, by the use of barks or extracts. This mordanting action is practiced on skins that have been previously unhaired and delimed, and is obtained by the action of different mordants used in dyeing, such as alum, certain salts of iron or aluminium, etc., but also frequently with acetate of aluminium diluted in an equal weight of water, and free, as far as possible, from sulphuric acid, salts of iron and pyroligneous substances that might discolor the leather.

The skins are immersed in this bath and allowed to remain from 28 to 48 hours, so as to become thoroughly impregnated with the mordant, and prepared to retain the tanning substances employed later.

After the above bath the skins are taken out and allowed to drain off, and are then placed in a tan liquor composed of water and tanning extracts, in the same proportions as used for the rapid tanning process. They are left in this liquor for 8 or 10 days, until tanning is complete, after which they are removed and again set to drain off, after which they are dried as usual.

In case it is desired to change the rapid tannage for the slow process, the skins are treated in the pits in the usual way.

Owing to the mordanting action they have undergone, the skins swell and absorb the tanning matter rapidly through all their substance. On the other hand, as this matter is not held in suspension in the skins as in present methods of rapid tanning, but are thoroughly fixed in the fibers, subsequent washing removes only the excess of tanning material used, without touching those that have been assimilated with the fibers.

To effect properly the fixing of the tannin, the skins should be frequently suspended and the liquor kept in a constant slow rotary movement, but not violently agitated, which would have the effect of injuring the skins. For this purpose a suction pump is used in the lower part of the tank and the liquor is discharged at the top.

The above process is applicable to all kinds of skins, varying the time of immersion according to their nature, thickness, etc.

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## THE SWELLING OF COLLOID JELLIES.

*By Henry Richardson Procter and John Arthur Wilson.*

In a recent publication[1] entitled "The Acid-Gelatin Equilibrium," the authors have explained the various peculiarities of the equilibria resulting when gelatin is immersed in solutions of acids of different strengths and concentrations. The object of the present paper is to show that the laws which were derived are applicable to the swelling and contracting by electrolytes of colloid jellies in general and to suggest working methods for the determination of the various factors of any given series of equi-

[1] *Transactions* Chemical Society (English), 1916, **109**, 307. This JOURNAL, 1916, XI, 261.

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libria with a view to utilizing the information so obtained, from a practical as well as theoretical standpoint.

Gelatin and hydrochloric acid combine to form a salt which is highly ionized into chloridion and a non-diffusible colloid cation, and a condition results in which, so long as the jelly phase and surrounding solution remain distinct, the concentration of diffusible ions in the jelly must always be greater than that in the external acid solution; and since the non-ionized acid is equal in both phases, this excess of ionic concentration determines, by its increase or decrease, the degree of swelling or contracting of the jelly mass. It will be shown presently that the laws governing this equilibrium apply to the swelling and contracting of any colloid jelly, if we assume that the colloid dissociates into a diffusible ion and a non-diffusible colloid ion, or that the colloid combines or reacts with an electrolyte forming a compound which is thus dissociated, and that the colloid jelly is permeable to all diffusible electrolytes and their ions concerned in the equilibria. In any given equilibrium two distinct phases will exist: that of the jelly and that of the solution surrounding it; and, although not equal, the concentration of any particular ion in one phase will bear a definite relation to its concentration in the other. The following system of notation has been adopted in order to simplify an otherwise rather complicated series of relations:

$x$ = sum of concentrations of positive *or* negative ions in the external solution.

$y$ = sum of concentrations in the jelly of *diffusible* ions with charges of the same sign as that of the colloid ion.

$z$ = sum of concentrations of ionized colloid molecules.

therefore $y + z$ = sum of concentrations in the jelly of *diffusible* ions with charges of opposite sign to that of the colloid ion.

$e$ = excess of concentration of *diffusible* ions of the jelly over that of the external solution.

The simplest case under consideration is that of a colloid which, when immersed in water, gives off a diffusible ion, at the same time retaining its jelly character. Let the compound be RS, which dissociates into the non-diffusible colloid ion $R^+$ and the diffusible anion $S'$. The anion will tend to diffuse outward into the surrounding water, and, being restrained by the electro-

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chemical attraction of the colloid cation, will exert upon the jelly mass an outward pull, causing it to swell, with the absorption of water, until the osmotic pressure of the anion is just counterbalanced by the cohesive elasticity of the jelly. At equilibrium $x = 0$, $y = 0$, and $z = e = [S']$. (If the osmotic pressure in the jelly were continually greater than the opposing cohesive forces, a colloidal solution would result). The degree of ionization of the colloid compound is the determining factor as regards the degree of swelling and, if we should add an electrolyte MN of such a nature that RN was ionized to quite a different degree from RS, the degrees of ionization of the various compounds formed would have to be taken into consideration. We shall, therefore, in the first instances, consider all the compounds to be practically totally ionized. If we now add some of the electrolyte MN, a change in the equilibrium is inevitable, for, as Donnan and Harris have shown,[1] the *products* of any pair of diffusible and oppositely-charged ions must be equal in the two phases. Some S′ ions must diffuse into the outer solution while $M^+$ and N′ diffuse into the jelly and equilibrium will again be established only when

$$\begin{cases} [M^+]_1 \times [N']_1 = [M^+]_2 \times [N']_2 \\ [M^-]_1 \times [S']_1 = [M^+]_2 \times [S']_2 \end{cases}$$

where $[M^+]_1$ signifies concentration of $M^+$ in the external solution and $[M^+]_2$ its concentration in the jelly. Adding

$$[M^+]_1 \times ([N']_1 + [S']_1) = [M^+]_2 \times ([N']_2 + [S']_2)$$

or (1) $$x^2 = y(y + z)$$

and since $e = [M^+]_2 + [N']_2 + [S']_2 - [M^+]_1 - [N']_1 - [S']_1$

(2) $$e = 2y + z - 2x.$$

and from (1) and (2) $$e = -2x + \sqrt{4x^2 + z^2}.$$

If MN does not combine or react with the colloid, its addition increases the value of $x$, but not of $z$, and consequently diminishes the value of $e$, and the greater the increase in concentration of the electrolyte MN, the greater the decrease of $e$. But $e$ is the measure of the force producing swelling and consequently, if the jelly possesses cohesive elasticity, the addition of any electrolyte MN will cause repression of the swelling of the jelly. All

[1] *Transactions* Chemical Society (English) 1911, **99**, 1575.

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binary electrolytes whose ionization can be considered practically total should produce the same degree of repression of swelling when added so as to produce equivalent concentrations provided they do not react chemically with the colloid.

The second case is that of a colloid which does not itself ionize to any appreciable extent when immersed in water, but which combines or reacts with an electrolyte forming an ionizing compound. Examples of this would be the combination of gelatin and HCl, in which a highly ionizable chloride of gelatin is formed or the neutralization of free carboxyl terminals of a protein molecule by NaOH, in which water and a highly ionizable sodium compound of the protein are formed. Let the colloid R, combine with the electroylte QS, forming the ionizing compound RS, $Q^+$ being partially removed from solution by entering into the colloid ion $R^+$. At equilibrium

$$[Q^+]_1 \times [S']_1 = [Q^+]_2 \times [S']_2$$

or $$x^2 = y(y + z)$$

and $$e = [Q^+]_2 + [S']_2 - [Q^+]_1 - [S']_1$$

or $$e = 2y + z - 2x$$

whence, as before, $$e = -2x + \sqrt{4x^2 + z^2}.$$

Before any of QS has been added $x = 0$, $z = 0$, and consequently $e = 0$; but, as we add QS, $x$ and $z$ assume finite values increasing $e$ and thus causing the jelly to swell. But this action is limited since the concentration of uncombined colloid molecules is decreasing, both because they are continually being converted into the colloid compound RS and because of their dilution due to swelling, thus giving $z$ a limiting maximum value, in which case

$$\lim_{x = \infty} \sqrt{4x^2 + z^2} = 2x$$

and therefore

$$\lim_{x = \infty} e = -2x + 2x = 0$$

from which it is evident that as $x$ is increased from zero, the value of $e$, and hence the increase in volume of the jelly, increases to a maximum and then decreases approaching zero asymptotically. This, of course, assumes that the value of $x$ may be increased indefinitely without destroying the colloid compound, which certainly is not always the case. In the equilibrium

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of gelatin and HCl, the concentration of acid, if increased sufficiently, will result in the hydrolysis of the gelatin, even reducing it to simple amino-acids, thus destroying the equilibrium, which at room temperature holds up to about $x = 0.3$N. Such decomposition is outside the scope of the present reasoning, which is concerned only with the regions of any series of experiments where decomposition of the colloid compound is practically nil.

If, at any stage of swelling of the colloid jelly by QS, we add some of the electrolyte MN, which does not combine or react with the colloid, according to the law of equality of products, we must have at equilibrium the following set of conditions:

$$\begin{cases} [Q^+]_1 \times [N']_1 = [Q^+]_2 \times [N']_2 \\ [Q^+]_1 \times [S']_1 = [Q^+]_2 \times [S']_2 \\ [M^+]_1 \times [N']_1 = [M^+]_2 \times [N']_2 \\ [M^+]_1 \times [S']_1 = [M^+]_2 \times [S']_2 \end{cases}$$

whence $([Q^+]_1 + [M^+]_1)([N']_1 + [S']_1) = ([Q^+]_2 + [M^+]_2)([N']_2 + [S']_2)$

or $$x^2 = y(y + z)$$

and $$e = 2y + z - 2x$$

whence $$e = -2x + \sqrt{4x^2 + z^2}$$

from which it follows that the addition of MN, since it cannot increase $z$, must diminish $e$, and consequently repress the swelling of the jelly.

The same line of reasoning can be extended to include any number of different electrolytes, whether all or only some combine with the colloid molecules forming ionizing compounds, and for electrolytes of any degree of ionization. In any case the same pair of equations will result, which can be reduced to

$$e = -2x + \sqrt{4x^2 + z^2}$$

but in this general case the curve for $e$ is not sharply defined since the variations of $z$ and $x$ are independent of one another. The curve is obviously one with a maximum, but may possess any number of maxima and minima before all of the colloid molecules have been converted into ionizing compounds, dependent upon the order and amounts in which the various electrolytes are added. The conversion of colloid molecules into ionizing compounds tends to increase $e$ and consequently to increase the

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swelling, while the addition of any electrolyte not combining or reacting with the colloid must produce contraction of the jelly. After all the colloid molecules have been converted into ionizing compounds, and no further combination takes place, the addition of any electrolyte must produce a degree of contraction of the jelly dependent upon the amount of the electrolyte added and its degree of ionization, provided its influence upon the ionizations of the other electrolytes concerned can be neglected.

If we differentiate with respect to $x$

$$\frac{de}{dx} = -2 + \frac{4x + z\frac{dz}{dx}}{\sqrt{4x^2 + z^2}}$$

As $z$ approaches constancy, $\frac{dz}{dx}$ approaches zero, and the value of $\frac{de}{dx}$ becomes negative, showing that the jelly is contracting. On the other hand, if $\frac{dz}{dx}$ should approach or become a finite constant, or should increase, the jelly would continually swell, since, if $z = ax$, $e = x\left(-2 + \sqrt{4 + a^2}\right) = Kx$. The swelling or contracting of the jelly is thus dependent upon the ratio of the rate of increase of $z$ to that of $x$.

All of the foregoing reasoning is based upon the assumption of the formation of an ionizing compound of the particular colloid under consideration, and whether or not this is so is left to experiment to decide. The equations derived are quantitative in character and form a logical conclusion from our hypothesis, and therefore present a basis of reasoning for the planning of series of experiments to decide not only the question of whether an ionizing compound of the colloid exists, or is formed, but many others, including the equivalent or molecular weight of the colloid, the nature of the compound formed, and the modulus of rigidity of the colloid jelly.

To illustrate the experimental manipulation we shall choose any colloid R which forms a jelly (such as gelatin), any acid HN and its neutral salt MN. We make up a series of acid solutions of increasing concentrations and into 100 cc. of each immerse 1 gram of R and allow them to stand long enough to reach equilibrium.

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If (as in the case of gelatin and HCl) we find that the jelly has swollen, with increasing concentration of acid, to a maximum and then contracted indefinitely, it suggests that R and HN have combined or reacted to form an ionizing compound, according to the reasoning given earlier in this paper. On the other hand, if we find that MN produces no swelling, but will contract the jelly swollen with acid according to the amount of salt added, it suggests that R and MN do not combine or react to form an ionizing compound. But this reasoning can easily be confirmed where the electrolytes and colloid compound are sufficiently highly ionized. We separate the swollen jelly from the acid solution, remove adhering acid by blotting gently, and, after weighing the blotted jelly, transfer it to a dry bottle and add the powdered salt MN to saturation. This acts as a great increase in $x$ and, since it does not produce more of the colloid compound, the swollen jelly contracts leaving the acid solution, which it had absorbed, surrounding it. The contracted jelly is then carefully blotted and weighed and the concentration of acid determined both in the solution which surrounded the jelly at equilibrium and that expelled by addition of salt. The volume of the external acid at equilibrium is determined by subtracting the weight of the swollen jelly from the total weight of acid and jelly, and the volume of the saturated salt solution by subtracting the weight of the contracted jelly from that of the swollen jelly, making the necessary corrections for the weight of and increase of volume due to the salt. The volume of solution still remaining in the jelly can be calculated from the weight of the contracted jelly and that of the dry jelly. This volume should be very small and, if so, we can assume, without great error, that the free acid it contains is of the same concentration as that in the saturated salt solution.

Let $a$ = concentration of initial acid,
$b$ = concentration of acid at equilibrium,
$c$ = concentration of free acid in the jelly,
$V'$ = volume of original acid solution,
$V''$ = volume of external solution at equilibrium,
$V'''$ = volume of solution absorbed by jelly,

then *quantity acid combined with colloid* $= V'a - V''b - V'''c$. This figure can be determined for any number of different

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strengths of acid and its curve should indicate the degree of combination of R and HN and lead to the derivation of the equivalent weight of the colloid, assuming it to be the weight which combines with the equivalent weight of the acid.

From $b$, knowing the degree of ionization of the acid, we can calculate $x$, and since $b - x$ represents the concentration of non-ionized acid, which is equal in both phases,

$$y = c - (b - x)$$

But, knowing $x$ and $y$, we can calculate all other variables, for if we solve our two fundamental equations simultaneously, we get

$$z = \frac{x^2 - y^2}{y}$$

$$e = \frac{(x - y)^2}{y}$$

From $z$ and the volume of the swollen jelly we can calculate the quantity of the *ionized* colloid compound, and since we know the total quantity of the colloid compound we can calculate its degree of ionization. The relation of $e$ to the increase in volume of the jelly determines the modulus of rigidity or bulk modulus of the colloid compound.

All the factors of the equilibrium could be determined easily enough if only the colloid could be obtained in a pure state and were not liable to decomposition, either through hydrolysis or by the added electrolytes, and all compounds concerned in the equilibria were sufficiently highly ionized. For example it is extremely difficult, if possible at all, to obtain gelatin which is quite free from inorganic matter and from products of hydrolytic decomposition. It combines with acids forming equilibria of the type described, but the experimental possibilities are limited by the fact that it is hydrolyzed by the stronger acid solutions. With weak acids, such as acetic, gelatin forms highly ionizable salts which repress the ionization of the free acid in the jelly to such an extent that the combination of acid and gelatin nears completion only at a very high total concentration of the acid, and for the same reason the difference between $x$ and $y$ is always relatively greater than with HCl, which makes the value of $e$ much greater since $e = \frac{(x - y)^2}{y}$. The swelling is great and the ten-

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dency to repression very small, so that hydrolysis of the gelatin begins before the swelling has shown any maximum. The repression of swelling by sodium acetate is much less complete than in the case of the chlorides because of the higher value for $e$ and the smaller degree of ionization of the salt. In the case of weak acids it is hardly possible to obtain the value of $y$, by the method described, with sufficient accuracy for the calculation of the variables $z$ and $e$, for relatively small errors in $y$ produce large errors in $z$ and $e$ as is shown by the curves in Figs. 1 and 2.

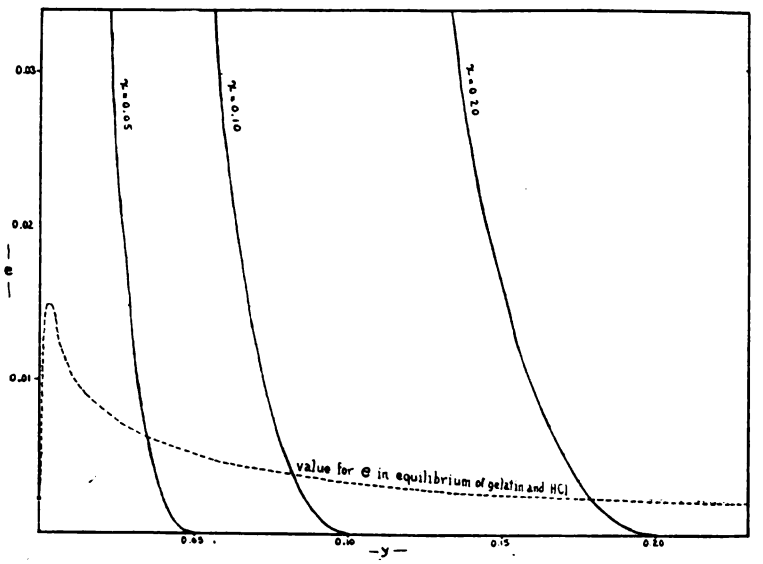


FIG. 1.

The significance of the curves will be made clear by the following example: If $x$ has been determined and found to be 0.20, then $z$ or $e$, as the case may be, must lie somewhere along the line designated by $x = 0.20$. The determination of $y$ now fixes the values of $z$ and $e$, but it will be seen that, because of the great slopes of the curves, any errors in determining $y$ will be multiplied in the calculations of $z$ and $e$; and so, where $y$ has not been determined with very great accuracy, the calculated values will show little or no tendency to form smooth curves. It was this fact that rendered our earlier attempts to find the curve for $e$

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in the acid-gelatin equilibrium so baffling. The dotted lines represent the curves for this equilibrium which were finally obtained by having recourse to other methods.

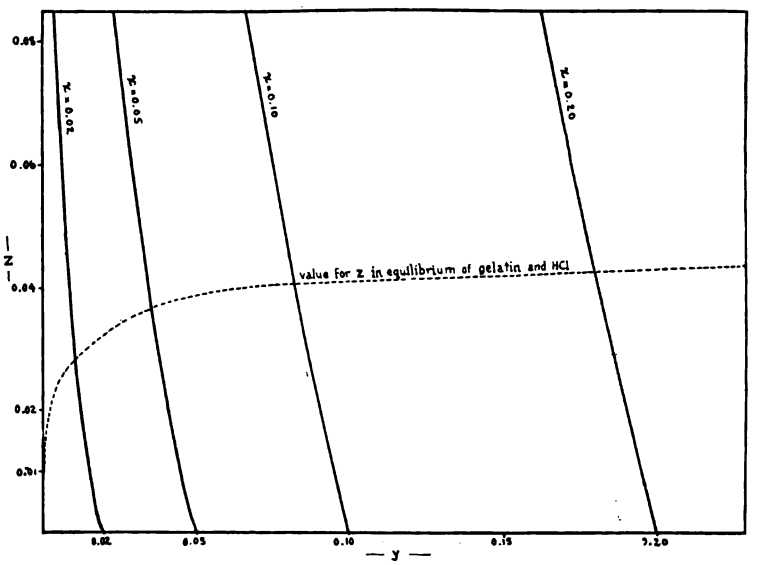


FIG. 2.

With perfectly pure colloids which have not undergone any decomposition during the manipulation, the matter is simple enough, but the presence of organic matter, and especially polypeptides and amino-acids, in acid or alkaline solutions to be titrated, renders the end-point too vague, considering the degree of accuracy required. But the various factors of almost any equilibrium can be approximated by determining a given variable by as many different methods as the conditions of the particular equilibrium will allow. For example, in the equilibrium of gelatin and HCl, the variables can be determined as mentioned above, but the difficulties in determining $y$ with great accuracy render the values calculated for $z$ and $e$ rather doubtful. But $y$ can be determined directly in the melted jelly by means of the hydrogen electrode and $(y + z)$, the total concentration of chloridion in the jelly, by means of the calomel electrode, and from these values $x$ and $e$ can be calculated, giving another set of values for

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all four variables. It was found in this case that the value for $(y + z)$ closely approximated the concentration of chloridion which would be produced if all the chlorides known to be present in the jelly were ionized to about the same extent as HCl, showing that the gelatin salt is highly ionized. This makes possible a third check upon the work, since the concentration of gelatin chloride, which we have determined by volumetric analysis, should be greater than $z$ by only a few per cent. A fourth check is outlined in our last paper (*loc. cit.*) and is applicable where all compounds concerned are highly ionized. It involves the use of $x$ and the volume of the swollen jelly, from which $y$, $z$, and $e$ can be calculated. A fifth check is possible with rigid jellies within the limits in which they obey Hooke's Law, *ut tensio sic vis*. Where V represents the increase in volume of the jelly and $k$ a constant corresponding to the bulk modulus of the jelly

$$e = k\mathrm{V}$$

from which, using our two fundamental equations,

$$y = \frac{2x + k\mathrm{V} - \sqrt{4k\mathrm{V}x + k^2\mathrm{V}^2}}{2}$$

$x$ is easily determined, V can be found by weighing and $k$ by solving any two sets of values.

Further information concerning the nature of the reaction or combination of colloid R and a binary electrolyte can be obtained by determining sets of values for $\mathrm{R}\frac{y}{z}$, where R represents the concentration of uncombined colloid molecules. If a compound is formed according to the equation $\mathrm{R} + \mathrm{MN} \rightleftharpoons (\mathrm{RM})^+ + \mathrm{N}'$, then $\mathrm{R}\frac{y}{z}$ represents the ionization-$k$ of the colloid cation. If the value for $\mathrm{R}\frac{y}{z}$ is found to be constant, another method is available for the determination of the equivalent or molecular weight of the colloid. R represents the total concentration of colloid molecules minus the concentration of molecules of the colloid compound. But if we have started with 1 gram of the colloid

$$\text{total conc. colloid molecules} = \frac{1000}{\mathrm{V} \times \text{equ. wt.}} \text{ gram equ. per litre,}$$

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where V represents the volume of swollen jelly in cubic centimeters. If we call the concentration of molecules of the colloid compound $(a + z)$, where $a$ represents the non-ionized portion, then

$$R = \frac{1000}{V_1 \times \text{equ. wt.}} - (a + z)$$

If $R \frac{y}{z}$ is constant, then for any two sets of values,

$$\frac{\left[\frac{1000}{V_1 \times \text{equ. wt.}} - (a_1 + z_1)\right] y_1}{z_1} = \frac{\left[\frac{1000}{V_2 \times \text{equ. wt.}} - (a_2 + z_2)\right]}{z_2}$$

or

$$\text{equivalent weight} = \frac{\frac{1000\ v_2\ z_1}{V_2} - \frac{1000\ y_1\ z_2}{V_1}}{y_2\ z_1\ (a_2 + z_2) - y_1\ z_2\ (a_1 + z_1)}$$

This equation holds true only provided $R \frac{y}{z}$ is constant and therefore furnishes a means of testing its constancy. Any number of determinations of equivalent weight can be made, by substituting different sets of values, and if all the determinations are practically equal $R \frac{y}{z}$ may be taken as constant and the equivalent weight as the correct one, which should check with the one obtained by means mentioned earlier in the paper. If $R \frac{y}{z}$ is not found to be constant, its curve should be plotted from results obtained from R, $y$, and $z$, but in this case the value of R would have to be obtained means of the equivalent weight obtained by the method first mentioned. The curve might suggest the nature of the reaction, whether a polyvalent colloid ion is formed, or the reaction is one of double decomposition and recombination, or possibly is a case of *adsorption* of one ion of the electrolyte by the colloid.

It will sometimes occur that the amount of electrolyte combined with the colloid is small compared with the total quantity of electrolyte present in the jelly, in which case it may prove

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very difficult to determine whether the quantity of combined electrolyte is increasing slightly or remains constant. This point can be settled by a method, the principle of which was discussed earlier in the paper. Suppose the colloid R combines with the electrolyte MN, forming a compound which ionizes into $(RM)^+$ and N′, but does not combine with the electrolyte QN which is ionized to practically the same extent as MN. If the quantity of combined electrolyte has become constant the addition of equivalent quantities of either MN or QN should produce exactly the same degree of repression of swelling, which can be determined accurately by weighing the jelly, while, if the quantity of combined electrolyte is still increasing, QN must necessarily produce a greater repression of swelling than MN, and the difference between the weights of the jellies in the two cases will be a measure of the rate of increase of combined electrolyte.

In all this work the question of temperature is one of vast importance and for the results of any series of experiments to be comparable the work must have been done at constant temperature. A sample of gelatin which will swell to twenty times its original volume at 8° may swell to double this amount at 18°, which is due to the diminution of the cohesive elasticity of the jelly. An increase in volume due to increase of $e$ is found, in the case of gelatin, to be completely reversible, but that due to increase of temperature appears not to be reversible. The fact that the degree of swelling of a given sample of gelatin is influenced by its volume at the moment of setting is probably due to analogous causes. This would indicate a non-reversible decrease of cohesive elasticity with increase of temperature, which would result, if the temperature were not kept constant, in the equilibrium approximating that which would result had the maximum temperature been maintained throughout. In the acid-gelatin equilibrium the volume was found to obey Hooke's Law very approximately; *i. e.*, the increase of volume at any fixed temperature varied directly as $e$, within the limits of experimental error, but for each temperature there was a different constant, corresponding to the bulk modulus, or modulus of rigidity of the jelly. An alteration in the bulk modulus will alter the relation existing between any pair of variables concerned in the equilibrium, which illus-

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trates the need for conducting all the experiments of any one series at exactly the same temperature.

The laws governing these equilibria have already been successfully applied to certain problems of swelling and contracting of hides in the tanning process and their application to problems of other industries is under consideration, but probably of equal importance is their application to physiological and medical problems.

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## THE DENATURING OF EGGS.*

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(1) A means of preventing the use of spoiled eggs in food materials.

(2) Denaturants which do not impair the value of eggs for tanning.

In the successful denaturing of spoiled eggs, a denaturant must be chosen (1) which will not only render the eggs inedible, but also food materials containing the denatured eggs inedible even though an attempt be made to cover or mask the denaturant, (2) which will not impair the value of the eggs as used in the tanning and finishing of leather, (3) which will not result in an objectionable color or odor in the finished leather, and (4) which will be inexpensive, readily obtainable, and which can be easily and uniformly applied.

In general there are two possible methods of denaturing eggs: (*a*) Denaturing in the shell; (*b*) Denaturing after removal from the shell.

In considering the possibility of successfully denaturing eggs in the shell it is self-evident that:

* Read at the Thirteenth Annual Meeting of the A. L. C. A., Atlantic City, June 3, 1916. Published by permission of the Secretary of Agriculture.

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1. The denaturant must penetrate the shell, or it may be removed by washing, the eggs be broken out and placed upon the market. (A case illustrating the above conditions is known.)
2. Special apparatus will be required to force the denaturant into the shell. The expense of denaturing will be thereby greatly increased.
3. The amount of denaturant forced through the shell will differ materially with different shells. Therefore with any given lot of eggs it will be impossible to ascertain when all eggs have been impregnated. Furthermore, it will be impossible to regulate the amount of denaturant which penetrates the shells.
4. The cost of shipping eggs out of the shell is less than that of shipping eggs in the shell. The necessary equipment and cost of breaking out eggs is relatively small.
5. There is little doubt that the loss due to decay during shipping will be less with the eggs which have been removed from the shell, denatured and preserved with 20 per cent. salt, than with eggs in the shell.

It was therefore decided to confine this work to an investigation of methods of denaturing eggs after they have been removed from the shell.

To obtain denaturants complying with the prescribed requirements, the experiments described below have been conducted.

## I. Preliminary Laboratory Baking Experiments Testing Various Denaturing Materials.

In order to determine whether or not certain materials would successfully denature eggs, several baking experiments were carried out. Sponge cakes were baked, using eggs to which a known percentage of denaturant (calculated on the weight of the eggs out of the shell) had been added. These cakes were then examined by taste and smell to learn if they were rendered inedible by the use of the denatured eggs.

In the first experiment, six tests were made using powdered dandelion root; powdered quassia; kerosene; fish oil; oil rosemary; and oil pennyroyal. Five per cent. by weight (calculated

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on the weight of the eggs used) of each denaturant was added to the eggs.

As a result of these experiments quassia and kerosene were considered promising. Pennyroyal and rosemary were successful as denaturants but are too expensive.

Before progressing further with the work it was decided to confer with tanners with regard to denaturants which would be suitable for tanners' eggs.

## II. Conferences with Tanners.

Eleven tanneries were visited. Seven of these which used tanners' egg yolk were asked to suggest materials which in their opinion might be used in tanners' egg yolk without being injurious to the finished leather. The information and suggestions given by the tanners may be summarized as follows:

Alum tanned leathers are the leathers in which egg yolk is most largely used. Alum tannage is applied to sheep and goat skins and horse hides. The sheep and goat skins are finished in grain, suede and mocha for glove leathers; horse hide leather is used for baseball covers.

*Quality of Egg Yolk Desired by the Tanner.*—The first grade yolk should be prepared from the eggs which are not too far decomposed to permit of the separation of yolks from whites. It should contain only a small amount of albumen, since this material makes the leather harsh and does not allow the nap of suede and mocha leathers to rise or stand. After the eggs are broken out and the whites removed, the yolks should be preserved by the addition of not less than 20 per cent. of salt.

Second grade tanners' yolk should contain such eggs as "heavy spots," "blood rings" and "white rots." It is impossible to make a very complete separation of the albumen from the yolk in these eggs. This is especially true in the case of "white rots." Some of the albumen may be removed by allowing the broken eggs to stand for several hours in a tank with a funnel shaped bottom carrying a stop-cock and then drawing off the whites after they have settled out. The egg yolk is put up in barrels for shipment.

Frozen and desiccated eggs have been experimented with by the tanners, and in all cases were reported as giving unsatisfactory results; it being claimed that the properties of the yolks or

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egg oil had been changed. The exact change which takes place is not definitely known. It may be due to the removal of water from the oil, thus causing the oil to be less easily emulsified. Many tanners claim that no other oil can be satisfactorily substituted for egg oil or egg yolk, in the manufacture of alum tanned glove leathers. The egg yolk used by the tanner varies in price according to the quality, from 5 to 12 cents per pound.

*Denaturants.*—The tanners were asked to suggest denaturing materials which would be unobjectionable to the tanning processes. Russian birch oil or brich tar oil (the oil obtained in the destructive distillation of white birch wood) was the material suggested and this was approved by all of the alum tanners visited. Many tanners use this oil in the preparation of certain kinds of leather in which the odor of Russian birch oil is desired. Other materials mentioned as possible denaturants were oil of mirbane, oil of pennyroyal, oil of sassafras, banana oil, sanitas and capsicum. Kerosene did not meet with the approval of the tanners because of the objectionable odor which might persist even in the finished gloves.

From the conference with the tanners the following conclusions were drawn:

*A.* Tanners do not use dried or frozen egg yolk.

*B.* Tanners wish egg yolk practically free from albumen.

*C.* Tanners in general approve the use of Russian birch oil as a denaturant.

### III. Further Laboratory Baking Experiments to Determine the Suitability of Materials Suggested as Denaturants.

Russian birch oil, oil of mirbane, quassia wood and cedar oil were tested in baking experiments. The results are given in Table C.

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RESULTS OF EXPERIMENT—C.

| Denaturant | Pecentage of denaturant used | Denatured | Remarks |
|---|---|---|---|
| Russian birch oil..... | 1.0 | + | Better than 0.5 per cent. |
| Russian birch oil..... | 0.5 | + | Not sufficient. |
| Mirbane..... | 1.0 | + | Unsatisfactory because mirbane is poisonous. |
| Birch oil and quassia .....0.1 and 0.5 | | + | Odor not objectionable, bitter from quassia. |
| Cedar oil from leaves.... ... | 1.0 | + | Not very objectionable but too expensive. |

## IV. COMMERCIAL BAKING EXPERIMENTS USING DENATURED EGGS, TO DETERMINE THE POSSIBILITY OF COVERING OR MASKING THE DENATURANTS USED.

Two quarts of fresh egg yolk were prepared by breaking out fresh eggs and separating yolks from whites. The yolks were mixed, divided into four parts, one pint each, labeled Nos. 1, 2, 3 and 4, and were denatured by the addition of 1 per cent. by weight of Russian birch oil, 0.5 per cent. by weight of Russian birch oil, 0.5 per cent. by weight of kerosene, and 0.5 per cent. by weight powdered quassia wood, respectively.

The denatured egg yolks prepared as described above were used by a reliable baking company in baking four 10-pound fruit cakes. The baking company was instructed to mask or cover the denaturants if possible. The resulting cakes were labeled by number and were tasted by about forty people. The opinions of the people were recorded, and the results of the test tabulated below.

Arranging the denaturants in such order that the most objectionable to taste is given first and the least objectionable to taste is given last, the following order is obtained:

*A*. 1.0 per cent. Russian birch oil.

*B*. 0.5 per cent. kerosene.

*C*. 0.5 per cent. Russian birch oil.

*D*. 0.5 per cent. powdered quassia wood.

From the results of these experiments it was concluded that *A* and *B* were denatured and that *C* and *D* required more of the denaturants to render them inedible.

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Conclusions from baking tests:

(1) That 1 or 2 per cent. of Russian birch oil will render egg yolk inedible, and also food materials which contain 7.0 per cent. or more of eggs so denatured will be rendered inedible.

(2) That 1 or 2 per cent. of kerosene will render egg yolk inedible.

(3) That 2 to 4 per cent. of powdered quassia wood will effectively denature egg yolk.

Having shown by baking experiments the efficiency of different denaturants in rendering eggs inedible, the next subject for consideration is the effect produced by these materials when the denatured eggs are employed commercially in the tanning of leather.

## V. Preparation and Denaturing of Egg Yolk on a Commercial Scale.

The breaking out and separating of the eggs were conducted at a plant in New York City. Eggs which would pass the food standard were used for this work, in order that it might be known that any injurious effects obtained in the treatment of the leather were due to the denaturant used rather than to the quality of the eggs.

The prepared yolk was divided into four parts, and labeled Nos. 1, 2, 3 and 4. Twenty per cent. by weight of salt was added to each. The four samples were then denatured by the addition of 2 per cent. by weight of Russian birch oil, 1 per cent. by weight of Russian birch oil, 2 per cent. by weight of kerosene, and 4 per cent. by weight of powdered quassia wood respectively. Each sample was then carefully mixed, allowed to stand over night, again mixed, divided into four parts of about 35 pounds each and put into the wooden casks.

## VI. Experiments at Tanneries Using Denatured Egg Yolk.

*General Process for Alum Tanned Skins.*—The dry salted skins are soaked, washed, unhaired by treatment with lime or lime and arsenic sulphide, fleshed, delimed, bated and washed.

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Pickled skins are degreased and washed. The skins are tanned by drumming in a mixture of flour, alum, salt, egg yolk (in some cases olive oil) and water. Depending upon the leather desired, they are drum, tray or brush colored. Just prior to or just after coloring, the skins are usually re-egged. After tanning or after tanning and coloring, the skins are dried, dampened back in sawdust, staked and finished. The details of the process vary in the different plants.

### Opinions Expressed by Tanners.

The following opinions were expressed by tanners who have used samples of the denatured egg yolk:

*Plant No. 1.*

". . . would state that we have tried the quassia wood, also the kerosene, and we find nothing objectionable to either.

"We did not try the birch oil as we were afraid that owing to the dark color of the yolk it might interfere with the light shades. However, we do not say that it would affect the color, but as we were putting through skins ordered for samples we did not care to take a chance."

Since receiving this letter, this plant prepared us a skin on which was used the yolk denatured with 2 per cent. birch oil. This skin was colored light pink and gave no evidence of injury to the color. They further state ". . . we find no bad effects from either the egg yolk denatured with birch oil or the quassia wood, both of which we have used," and ". . . if there was any objection to using either of the above mentioned it would certainly appear in these colors."

*Plant No. 2.*

"We beg to say that, in our opinion, the egg yolk denatured with birch oil is best suited for glove leather. It left no objectionable odor, nor did it destroy any of the nourishing action of the egg yolk, and we are able to get the same color as where the skins had been treated with egg yolk not denatured. We believe the birch oil will not cause any difficulty in obtaining white leather.

"The skins in which kerosene was used as a denaturant seemed

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to finish harsher and not as pliable as those in which the denaturant was birch oil. The color, if anything, was somewhat improved. In our opinion, this was more than offset by the harshness of the stock as the kerosene seemed to cut the animal grease of the skin.

"The skins in which quassia wood was used as a denaturant were, in our opinion, not as soft, nor did they finish as well as the skins tried with the other two denaturants.

"In our opinion, therefore, there would be no objection by the glove leather manufacturers to the use of birch oil (at least in the quantity used in the trial sample), as a denaturant for egg yolk to be used in the manufacture of fine glove leathers."

*Plant No. 3.*

"As far as we are able to judge the sample lot of skins put through with egg yolk, you sent here for us to experiment with, has turned out satisfactory, and the stock is in no way damaged, due to the denaturing process you have put the eggs through."

*Plant No. 4.*

"In our opinion the results obtained on the skins egged in the egg yolk denatured with birch oil are preferable to the skins egged in either the egg yolk denatured with kerosene or quassia bark. You will find upon examination that the two skins marked No. 1 and No. 2 are brighter and more uniform in color and appearance and finish better than the skins egged with either kerosene or quassia bark in the egg.

"So far as we could judge from the results obtained on this sample lot we feel satisfied with the results obtained on skins No. 1 and No. 2, but we do not consider the results on skins No. 3 and No. 4 satisfactory."

*Plant No. 5.*

". . . we tanned four lots of skins with alum using egg yolk which had been denatured by you and sent to us.

"During the drying of these skins they were subjected to a rather high temperature and all the kerosene and birch oil odor was driven off. On examination of the finished skins we can find no difference in the character or appearance of the leather. We do not feel that we can approve of the use of kerosene as a

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denaturer because of the fire risk to the person denaturing the eggs and its presence in the tannery. It might also in the case of coloring leather have some influence on the resulting leather. In the case of birch oil it would be desirable, if that is used, to keep the quantity as small as possible because in cases where the leather is not subjected to the temperature as high as we have in drying these skins, more of the birch oil odor might be left in the leather in quantities sufficient to make it undesirable.

". . . you may find one skin to be slightly more yellow than the others, but the average of the whole lot would not be different from that of the others."

From experiments carried on at five tanneries using egg yolk denatured with (1) Russian birch oil, (2) kerosene, (3) quassia wood, results have been obtained which indicate that no material harm would come to leathers prepared with any of the above denatured egg yolks.

The yolk which was denatured with 2 per cent. kerosene is by far the best appearing yolk of the four samples denatured. Although no serious harm was done the leather in the experiments carried out, there are several reasons why this material would not be entirely satisfactory as a denaturant. There would be considerable fire risk entailed in the plant where the yolk was prepared, but more especially in the tannery where the yolk was used. In several cases the leather obtained, when yolk denatured with kerosene was employed, was harsher to the "feel" than the normal leather. It appeared that the kerosene has a solvent action on the animal grease. The yolk denatured with kerosene according to some tanners gave a little better color, but this was more than offset by the harsh "feel."

The yolk denatured with quassia wood caused no noticeable injury to the leather. This yolk, however, did not seem to appeal to the tanners as did the one denatured with birch oil.

The preference of the tanners seems to favor the yolk denatured with birch oil. There is no case recorded in which the yolk containing 2 per cent. of birch oil worked any injury. To tanners who have not experimented with yolk denatured with birch oil, the dark color of the prepared yolk may result in an unwarranted prejudice against this denaturing material. Inasmuch, however, as it has been possible to obtain normally white

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leathers and leathers dyed in delicate colors without difficulty, when using yolk denatured with birch oil, and since no objectionable odor has been obtained in the finished leathers, there appears to be at present no real objection to the use of this material in the amounts specified.

The cost of the different denaturants varies with market conditions and is now increased because of the war. Under normal conditions the approximate cost would be: birch oil, 10 cents per pound in barrel lots; kerosene, 10 to 15 cents per gallon (6.6 pounds); powdered quassia wood, 5 cents per pound. At these prices the cost of denaturing 100 pounds of yolk (worth from $6 to $12) would be for the birch oil 2 per cent., 20 cents; for kerosene 2 per cent., 4 cents; and for the quassia wood 4 per cent., 20 cents.

At the present time it is difficult to obtain Russian birch tar oil. There appears to be no reason why birch tar oil should or could not be prepared in this country. It has been suggested that the petroleum product called "Power Distillate" be substituted in place of the Russian birch tar oil during the present shortage. Laboratory baking experiments with "Power Distillate" have demonstrated that it will successfully render eggs inedible. But no experiments using eggs denatured with this material have been carried out at the tanneries.

The following specifications and methods for the examination of birch tar oil and "power distillate" have been prepared:

### Specifications for Birch Tar Oil for Denaturing Eggs and Egg Products.

*Specific Gravity.*—At 20° C. Shall be not less than 0.925 nor more than 0.960.

*Paraffin Bodies.*—Shall not exceed 20 per cent. by volume.

*Distillation.*—The quantity distilling below 250° C. shall not exceed 30 per cent. by volume. The quantity distilling between 250° and 350° C. shall not exceed 65 per cent. by volume. The quantity distilling above 350° C. shall not exceed 60 per cent. by volume.

*Denaturing Value.*—Shall meet the requirements specified under method.

*Odor and Taste.*—Shall be characteristic of birch tar oil.

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## Methods for the Examination of Birch Tar Oil to be Used for Denaturing Eggs and Egg Products.

### *Methods for Paraffin Bodies in Birch Tar Oil.*

Run 20 cc. of 38 times normal sulphuric acid into a Babcock bottle, stopper, and place in ice water, cool, add 5 cc. of birch tar oil, again cool, and gradually mix the contents, cooling from time to time (the temperature should not be allowed to rise materially), and when the mixture no longer warms up after shaking, agitate thoroughly. Then place the bottle in a water bath in which the water is on a level with the acid and heat to from 60° to 65° C. in the course of from five to ten minutes, keeping the contents thoroughly mixed by vigorously shaking six or seven times. Do not stopper the bottle after the birch tar oil has been added, as it may explode.

Cool to room temperature, add ordinary sulphuric acid until the contents rise in the graduated portion of the neck, and whirl in a centrifuge at 1,200 revolutions per minute for three or four minutes, or allow to stand over night, and read the amount of supernatant liquid.

When a small amount of adulterant has been added, it is preferable to use a centrifugal machine, reading the refractive index of the upper portion of the residue immediately, as the paraffin bodies and residual birch tar oil alternation product are thus stratified, the low reading paraffin oil constituting the upper portion. A capillary pipette is used in transferring a small portion of the residual oil to the refractometer.

As the destruction of the unsaturated components of the birch tar oil depends upon its contact with sulphuric acid, which in turn is dependent upon the minuteness of the birch tar oil particles suspended in the acid, it follows, and this is convincingly borne out by experience, that thorough mixing is one of the essential features of the method.

### *Method of Distillation for Birch Tar Oil.*

*Apparatus.*—Heating Bath: Prepare a basket of wire gauze which will surround the bulb of the distilling flask. Place the

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flask in the gauze basket and set the basket on an ordinary wire gauze. Distill with an open flame.

Distilling Flask: Comparable results can only be obtained in distillation by always using flasks of the same dimensions. The flask found most satisfactory in this work is an ordinary 300 cc. flask, 8 cm. in diameter, with the side tube 8 cm. from the main bulb, and the neck extending 8 cm. above the side tube. The neck is 2 cm. in diameter and the side tube is 5 cm.

Condenser and Receivers: Use an ordinary 15-inch condenser and graduated cylinder for receiving the distillate.

*Distillation.*—Place 200 cc. of the birch tar oil and several small pieces of pumice in the distilling flask, connect with the condenser, and set the distilling flask in the bath. Stopper the distilling flask with a cork through which passes two standardized thermometers graduated from 245° to 305° C. and from 305° to 360° C. respectively. The mercury bulbs are placed opposite the side tube and the 300° and 350° C. marks must be below the cork. Heat the bath slowly and when distillation begins regulate the heat so that the oil distills at the rate of two drops per second. When the thermometer reaches 250° C. remove the first cylinder and replace with a second. Replace the first thermometer by a short piece of glass rod and continue distillation until the thermometer records 350° C. Discontinue distillation, measure each fraction and determine its refractive index.

### *Method of Determining Denaturing Value.*

Weigh 5.0 grams of the denaturant under examination into a 100 cc. volumetric flask, make to volume with 95 per cent. alcohol and mix thoroughly. Weigh out separately, 70 grams of sugar, 25 grams of lard, 100 grams of flour, 7.5 grams of baking powder and 1.5 grams of salt (NaCl). Add 10 cc. of the alcoholic solution of the denaturant and 6 cc. of lemon extract to the lard and sugar and thoroughly mix. By sifting or otherwise thoroughly mix the flour, salt and baking powder. With constant stirring, gradually add 80 cc. of water and the flour mixture to the lard mixture. Place this batter in two shallow tins and bake from one-half to three-quarters of an hour at 190° C.

The baked product thus obtained shall possess a decided odor characteristic of the specified denaturant and shall be inedible.

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## Specifications for Petroleum Oil "Power Distillate" for Denaturing Eggs and Egg Products.

The power distillate used for denaturing eggs and egg products shall conform to the following specifications.

*Specific Gravity.*—At 20° C. Shall be not lower than 0.816.

*Flash Point* (Open Cup).—Shall be not lower than 75° C.

*Boiling Point.*—Shall be not lower than 205° C.

*Denaturing Value.*—Shall meet all requirements specified under methods given for birch tar oil.

*Odor and Taste.*—Shall be characteristic of the fraction of petroleum oil known as power distillate.

## Suggested Procedure for the Commercial Denaturing of Eggs and Egg Yolk.

The eggs to be denatured should first be broken and the liquid contents removed from the shell. In the preparation of tanners' egg yolk, the whites and yolks should be separated at the time of breaking out.

### *Suggested Treatment of Liquid Eggs and Egg Yolk.*

To a weighed quantity of the material to be denatured, in a barrel or similar suitable container, add 2 per cent. by weight of birch tar oil or of power distillate.

Thorough mixing is very essential. Thoroughly mix the eggs and denaturant in a revolving drum or barrel churn for ten or fifteen minutes or, in the absence of a mechanical apparatus, stir with a paddle or mixing ladle until the denatured product is uniform in appearance. This will require ten to fifteen minutes constant stirring.

A preservative is usually added to tanner's egg yolk. It is customary to add 15 to 20 per cent. by weight of common salt, which meets the general approval of the tanners.

## Summary.

1. From careful consideration of the very evident facts already mentioned, and results of brief experiments, it is believed to be impracticable to denature eggs in the shell.

2. Baking experiments have demonstrated that 2 per cent. by weight of birch tar oil can be successfully used to render eggs inedible.

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3. Eggs denatured with 2 per cent. of birch tar oil and used in the preparation of food materials, in amounts representing not less than 7.0 per cent. of the total weight of the ingredients used, render these food materials inedible.

4. Experiments at tanneries using egg yolk denatured with 2 per cent. by weight of birch tar oil, on a commercial scale, have failed to show any injuries to color, odor or quality of the resulting leather. White and delicately colored leathers have been prepared using this material.

5. It has been found that 2 per cent. by weight of "power distillate" will serve as a substitute denaturant in rendering eggs and food materials inedible. But experiments with this material at the tannery to determine its effect on leather have not been conducted.

### Conclusion.

Since birch tar oil, under normal trade conditions, fulfils all of the requirements of a successful denaturant for eggs, it has been recommended as the official denaturant for spoiled eggs.

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## TABLES SHOWING THE RELATION BETWEEN SPECIFIC GRAVITY, PER CENT. TOTAL SOLIDS AND TANNINS IN EXTRACTS.

*By Oskar Riethof.*

It is of value to the extract manufacturer to be able to tell, by a glance at a table, to what strength he has to evaporate an extract in order to get a product of a certain percentage of tannin. This depends, in the first place, upon the purity of the liquor, but inasmuch as this factor is nearly alike for an established process or can be obtained by analysis, the table will show how much the extract in question has to be diluted or strengthened in order to contain a certain percentage of tannin.

The specific gravity as marked in the tables was taken at 15° Celsius and it was found that the correction for the temperature at which the extract is tested when in the last effect—at 25 inches vacuum 128° F. is, for hemlock extract, 4° and for chestnut extract 5° Twaddell.

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## CHESTNUT EXTRACT.

| Degree Twaddell | Per cent. Total Solids | Purity, per cent. | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 |
| | | Per cent. tannin | | | | | | | | | | | | | | | | | | | | |
| 33.0 | 34.1 | 18.8 | 19.1 | 19.4 | 19.8 | 20.1 | 20.5 | 20.8 | 21.1 | 21.5 | 21.8 | 22.2 | 22.5 | 22.8 | 23.2 | 23.5 | 23.9 | 24.2 | 24.5 | 24.9 | 25.2 | 25.6 |
| 33.5 | 34.5 | 19.0 | 19.3 | 19.7 | 20.0 | 20.3 | 20.7 | 21.0 | 21.4 | 21.7 | 22.1 | 22.4 | 22.8 | 23.1 | 23.4 | 23.8 | 24.1 | 24.5 | 24.8 | 25.2 | 25.5 | 25.9 |
| 34.0 | 34.8 | 19.2 | 19.5 | 19.9 | 20.2 | 20.6 | 20.9 | 21.3 | 21.6 | 22.0 | 22.3 | 22.7 | 23.0 | 23.4 | 23.7 | 24.1 | 24.4 | 24.7 | 25.1 | 25.4 | 25.8 | 26.1 |
| 34.5 | 35.2 | 19.4 | 19.7 | 20.1 | 20.4 | 20.8 | 21.1 | 21.5 | 21.8 | 22.2 | 22.5 | 22.9 | 23.2 | 23.6 | 23.9 | 24.3 | 24.7 | 25.0 | 25.4 | 25.7 | 26.1 | 26.4 |
| 35.0 | 35.6 | 19.6 | 19.9 | 20.3 | 20.6 | 21.0 | 21.4 | 21.7 | 22.1 | 22.4 | 22.8 | 23.1 | 23.5 | 23.9 | 24.2 | 24.6 | 24.9 | 25.3 | 25.6 | 26.0 | 26.3 | 26.7 |
| 35.5 | 36.0 | 19.8 | 20.1 | 20.5 | 20.9 | 21.2 | 21.6 | 21.9 | 22.3 | 22.7 | 23.0 | 23.4 | 23.7 | 24.1 | 24.5 | 24.8 | 25.2 | 25.5 | 25.9 | 26.3 | 26.6 | 27.0 |
| 36.0 | 36.3 | 20.0 | 20.4 | 20.7 | 21.1 | 21.4 | 21.8 | 22.2 | 22.5 | 22.9 | 23.3 | 23.6 | 24.0 | 24.3 | 24.7 | 25.1 | 25.4 | 25.8 | 26.2 | 26.5 | 26.9 | 27.3 |
| 36.5 | 36.7 | 20.2 | 20.6 | 20.9 | 21.3 | 21.7 | 22.0 | 22.4 | 22.8 | 23.1 | 23.5 | 23.9 | 24.2 | 24.6 | 25.0 | 25.3 | 25.7 | 26.1 | 26.4 | 26.9 | 27.2 | 27.5 |
| 37.0 | 37.1 | 20.4 | 20.8 | 21.1 | 21.5 | 21.9 | 22.3 | 22.6 | 23.0 | 23.4 | 23.7 | 24.1 | 24.4 | 24.9 | 25.2 | 25.6 | 26.0 | 26.3 | 26.7 | 27.1 | 27.5 | 27.8 |
| 37.5 | 37.5 | 20.6 | 21.0 | 21.4 | 21.7 | 22.1 | 22.5 | 22.9 | 23.2 | 23.6 | 24.0 | 24.4 | 24.7 | 25.1 | 25.5 | 25.9 | 26.2 | 26.6 | 27.0 | 27.4 | 27.7 | 28.1 |
| 38.0 | 37.8 | 20.8 | 21.2 | 21.6 | 22.0 | 22.3 | 22.7 | 23.1 | 23.5 | 23.8 | 24.2 | 24.6 | 25.0 | 25.4 | 25.7 | 26.1 | 26.5 | 26.9 | 27.2 | 27.6 | 28.0 | 28.4 |
| 38.5 | 38.2 | 21.0 | 21.4 | 21.8 | 22.2 | 22.6 | 22.9 | 23.3 | 23.7 | 24.1 | 24.5 | 24.8 | 25.2 | 25.6 | 26.0 | 26.4 | 26.8 | 27.1 | 27.5 | 27.9 | 28.3 | 28.7 |
| 39.0 | 38.6 | 21.2 | 21.6 | 22.0 | 22.4 | 22.8 | 23.2 | 23.5 | 23.9 | 24.3 | 24.7 | 25.1 | 25.5 | 25.9 | 26.2 | 26.6 | 27.0 | 27.4 | 27.8 | 28.2 | 28.6 | 28.9 |
| 39.5 | 39.0 | 21.4 | 21.8 | 22.2 | 22.6 | 23.0 | 23.4 | 23.8 | 24.2 | 24.6 | 24.9 | 25.3 | 25.7 | 26.1 | 26.5 | 26.9 | 27.3 | 27.7 | 28.1 | 28.5 | 28.8 | 29.2 |
| 40.0 | 39.3 | 21.6 | 22.0 | 22.4 | 22.8 | 23.2 | 23.6 | 24.0 | 24.4 | 24.8 | 25.2 | 25.6 | 26.0 | 26.4 | 26.8 | 27.1 | 27.5 | 27.9 | 28.3 | 28.7 | 29.1 | 29.5 |
| 40.5 | 39.7 | 21.9 | 22.2 | 22.6 | 23.0 | 23.4 | 23.8 | 24.2 | 24.6 | 25.0 | 25.4 | 25.8 | 26.2 | 26.6 | 27.0 | 27.4 | 27.8 | 28.2 | 28.6 | 29.0 | 29.4 | 29.8 |
| 41.0 | 40.1 | 22.1 | 22.5 | 22.9 | 23.3 | 23.7 | 24.1 | 24.5 | 24.9 | 25.3 | 25.7 | 26.1 | 26.5 | 26.9 | 27.3 | 27.7 | 28.0 | 28.5 | 28.9 | 29.3 | 29.7 | 30.1 |
| 41.5 | 40.5 | 22.3 | 22.7 | 23.1 | 23.5 | 23.9 | 24.3 | 24.7 | 25.1 | 25.5 | 25.9 | 26.3 | 26.7 | 27.1 | 27.5 | 27.9 | 28.3 | 28.7 | 29.1 | 29.5 | 30.0 | 30.4 |
| 42.0 | 40.8 | 22.5 | 22.9 | 23.3 | 23.7 | 24.1 | 24.5 | 24.9 | 25.3 | 25.7 | 26.1 | 26.6 | 27.0 | 27.4 | 27.8 | 28.2 | 28.6 | 29.0 | 29.4 | 29.8 | 30.2 | 30.6 |
| 42.5 | 41.2 | 22.7 | 23.1 | 23.5 | 23.9 | 24.3 | 24.7 | 25.1 | 25.5 | 25.9 | 26.4 | 26.7 | 27.2 | 27.6 | 28.0 | 28.4 | 28.8 | 29.2 | 29.6 | 30.0 | 30.4 | 30.9 |
| 43.0 | 41.6 | 22.9 | 23.3 | 23.7 | 24.1 | 24.5 | 25.0 | 25.4 | 25.8 | 26.2 | 26.6 | 27.0 | 27.5 | 27.9 | 28.3 | 28.7 | 29.1 | 29.5 | 29.9 | 30.4 | 30.8 | 31.2 |
| 43.5 | 42.0 | 23.1 | 23.5 | 23.9 | 24.3 | 24.8 | 25.2 | 25.6 | 26.0 | 26.4 | 26.9 | 27.3 | 27.7 | 28.1 | 28.5 | 29.0 | 29.4 | 29.8 | 30.2 | 30.6 | 31.1 | 31.5 |
| 44.0 | 42.3 | 23.3 | 23.7 | 24.1 | 24.6 | 25.0 | 25.4 | 25.8 | 26.3 | 26.7 | 27.1 | 27.5 | 27.9 | 28.4 | 28.8 | 29.2 | 29.6 | 30.1 | 30.5 | 30.9 | 31.3 | 31.8 |
| 44.5 | 42.7 | 23.5 | 23.9 | 24.4 | 24.8 | 25.2 | 25.6 | 26.1 | 26.5 | 26.9 | 27.3 | 27.8 | 28.2 | 28.6 | 29.1 | 29.5 | 29.9 | 30.3 | 30.8 | 31.1 | 31.6 | 32.0 |
| 45.0 | 43.1 | 23.7 | 24.1 | 24.6 | 25.0 | 25.4 | 25.9 | 26.3 | 26.7 | 27.2 | 27.6 | 28.0 | 28.4 | 28.9 | 29.3 | 29.7 | 30.2 | 30.6 | 31.0 | 31.5 | 31.9 | 32.3 |
| 45.5 | 43.5 | 23.9 | 24.3 | 24.8 | 25.2 | 25.7 | 26.1 | 26.5 | 27.0 | 27.4 | 27.8 | 28.3 | 28.7 | 29.1 | 29.6 | 30.0 | 30.4 | 30.9 | 31.3 | 31.7 | 32.2 | 32.6 |
| 46.0 | 43.8 | 24.1 | 24.6 | 25.0 | 25.4 | 25.9 | 26.3 | 26.8 | 27.2 | 27.6 | 28.1 | 28.5 | 28.9 | 29.4 | 29.8 | 30.3 | 30.7 | 31.1 | 31.6 | 32.0 | 32.4 | 32.9 |
| 46.5 | 44.2 | 24.3 | 24.8 | 25.2 | 25.7 | 26.1 | 26.5 | 27.0 | 27.4 | 27.9 | 28.3 | 28.7 | 29.2 | 29.6 | 30.1 | 30.5 | 31.0 | 31.4 | 31.8 | 32.3 | 32.7 | 33.2 |
| 47.0 | 44.6 | 24.5 | 25.0 | 25.4 | 25.9 | 26.3 | 26.8 | 27.2 | 27.7 | 28.1 | 28.5 | 29.0 | 29.4 | 29.9 | 30.3 | 30.8 | 31.2 | 31.7 | 32.1 | 32.6 | 33.0 | 33.4 |
| 47.5 | 45.0 | 24.7 | 25.2 | 25.6 | 26.1 | 26.5 | 27.0 | 27.4 | 27.9 | 28.3 | 28.8 | 29.2 | 29.7 | 30.1 | 30.6 | 31.0 | 31.5 | 31.9 | 32.4 | 32.8 | 33.3 | 33.7 |
| 48.0 | 45.3 | 24.9 | 25.4 | 25.8 | 26.3 | 26.8 | 27.2 | 27.7 | 28.1 | 28.6 | 29.0 | 29.5 | 29.9 | 30.4 | 30.8 | 31.3 | 31.7 | 32.2 | 32.6 | 33.1 | 33.6 | 34.0 |
| 48.5 | 45.7 | 25.2 | 25.6 | 26.1 | 26.5 | 27.0 | 27.4 | 27.9 | 28.3 | 28.8 | 29.3 | 29.7 | 30.2 | 30.6 | 31.1 | 31.5 | 32.0 | 32.4 | 32.9 | 33.3 | 33.8 | 34.2 |
| 49.0 | 46.1 | 25.4 | 25.8 | 26.3 | 26.7 | 27.2 | 27.7 | 28.1 | 28.6 | 29.0 | 29.5 | 30.0 | 30.4 | 30.9 | 31.3 | 31.8 | 32.3 | 32.7 | 33.2 | 33.7 | 34.1 | 34.6 |

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## CHESTNUT EXTRACT.—(*Continued*)

| Degrees Twaddell | Per cent. total solids | Purity, per cent. | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 |
| | | Per cent. tannin | | | | | | | | | | | | | | | | | | | | |
| 49.5 | 46.5 | 25.6 | 26.0 | 26.5 | 27.0 | 27.4 | 27.9 | 28.4 | 28.8 | 29.3 | 29.7 | 30.2 | 30.7 | 31.1 | 31.6 | 32.1 | 32.5 | 33.0 | 33.5 | 33.9 | 34.4 | 34.9 |
| 50.0 | 46.8 | 25.8 | 26.2 | 26.7 | 27.2 | 27.6 | 28.1 | 28.6 | 29.0 | 29.5 | 30.0 | 30.5 | 30.9 | 31.4 | 31.9 | 32.3 | 32.8 | 33.2 | 33.7 | 34.2 | 34.7 | 35.1 |
| 50.5 | 47.2 | 26.0 | 26.4 | 26.9 | 27.4 | 27.9 | 28.3 | 28.8 | 29.3 | 29.8 | 30.2 | 30.7 | 31.2 | 31.6 | 32.1 | 32.6 | 33.1 | 33.5 | 34.0 | 34.5 | 34.9 | 35.4 |
| 51.0 | 47.6 | 26.2 | 26.7 | 27.1 | 27.6 | 28.1 | 28.6 | 29.0 | 29.5 | 30.0 | 30.5 | 30.9 | 31.4 | 31.9 | 32.4 | 32.8 | 33.3 | 33.8 | 34.3 | 34.7 | 35.2 | 35.7 |
| 51.5 | 48.0 | 26.4 | 26.9 | 27.3 | 27.8 | 28.3 | 28.8 | 29.3 | 29.7 | 30.2 | 30.7 | 31.2 | 31.7 | 32.1 | 32.6 | 33.1 | 33.6 | 34.1 | 34.5 | 35.0 | 35.5 | 36.0 |
| 52.0 | 48.3 | 26.6 | 27.1 | 27.6 | 28.0 | 28.5 | 29.0 | 29.5 | 30.0 | 30.5 | 30.9 | 31.4 | 31.9 | 32.4 | 32.9 | 33.4 | 33.8 | 34.3 | 34.8 | 35.3 | 35.8 | 36.3 |
| 52.5 | 48.7 | 26.8 | 27.3 | 27.8 | 28.3 | 28.7 | 29.2 | 29.7 | 30.2 | 30.7 | 31.2 | 31.7 | 32.2 | 32.6 | 33.1 | 33.6 | 34.1 | 34.6 | 35.1 | 35.6 | 36.1 | 36.5 |
| 53.0 | 49.1 | 27.0 | 27.5 | 28.0 | 28.5 | 29.0 | 29.5 | 29.9 | 30.4 | 30.9 | 31.4 | 31.9 | 32.4 | 32.9 | 33.4 | 33.9 | 34.4 | 34.9 | 35.3 | 35.8 | 36.3 | 36.8 |
| 53.5 | 49.5 | 27.2 | 27.7 | 28.2 | 28.7 | 29.2 | 29.7 | 30.2 | 30.7 | 31.2 | 31.7 | 32.2 | 32.7 | 33.1 | 33.6 | 34.1 | 34.6 | 35.1 | 35.6 | 36.1 | 36.6 | 37.1 |
| 54.0 | 49.8 | 27.4 | 27.9 | 28.4 | 28.9 | 29.4 | 29.9 | 30.4 | 30.9 | 31.4 | 31.9 | 32.4 | 32.9 | 33.4 | 33 9 | 34.4 | 34.9 | 35.4 | 35.9 | 36.4 | 36.9 | 37.4 |
| 54.5 | 50.2 | 27.6 | 28.1 | 28.6 | 29.1 | 29.6 | 30.1 | 30.6 | 31.1 | 31.6 | 32.1 | 32.7 | 33.2 | 33.7 | 34.2 | 34.7 | 35.2 | 35.7 | 36.2 | 36.7 | 37.2 | 37.7 |
| 55.0 | 50.6 | 27.8 | 28.3 | 28.8 | 29.3 | 29.9 | 30.4 | 30.9 | 31.4 | 31.9 | 32.4 | 32.9 | 33.4 | 33.9 | 34.4 | 34.9 | 35.4 | 35 9 | 36.4 | 36.9 | 37.4 | 37.9 |
| 55.5 | 51.0 | 28.0 | 28.5 | 29.1 | 29.6 | 30.1 | 30.6 | 31.1 | 31.6 | 32.1 | 32.6 | 33.1 | 33.6 | 34.2 | 34.7 | 35.2 | 35.7 | 36.2 | 36.7 | 37.2 | 37.7 | 38.2 |
| 56.0 | 51.3 | 28.2 | 28.8 | 29.3 | 29.8 | 30.3 | 30.8 | 31.3 | 31.8 | 32.3 | 32.9 | 33 4 | 33.9 | 34.4 | 34.9 | 35.4 | 35.9 | 36.5 | 37.0 | 37.5 | 38.0 | 38.5 |
| 56.5 | 51.7 | 28.5 | 29.0 | 29.5 | 30.0 | 30.5 | 31.0 | 31.6 | 32.1 | 32.6 | 33.1 | 33.6 | 34.1 | 34.7 | 35.2 | 35.7 | 36.2 | 36.7 | 37.2 | 37.8 | 38.3 | 38.8 |
| 57.0 | 52.1 | 28.7 | 29.2 | 29.7 | 30.2 | 30.7 | 31.3 | 31.8 | 32.3 | 32.8 | 33.3 | 33.9 | 34.4 | 34.9 | 35.4 | 36.0 | 36.5 | 37.0 | 37.5 | 38.0 | 38.6 | 39.1 |
| 57.5 | 52.5 | 28.9 | 29.4 | 29.9 | 30.4 | 31.0 | 31.5 | 32.0 | 32.5 | 33.1 | 33.6 | 34.1 | 34.6 | 35.2 | 35.7 | 36.2 | 36.7 | 37.3 | 37.8 | 38.3 | 38.8 | 39.4 |
| 58.0 | 52.8 | 29.1 | 29.6 | 30.1 | 30.7 | 31.2 | 31.7 | 32.2 | 32.8 | 33.3 | 33.8 | 34.4 | 34.9 | 35.4 | 35.9 | 36.5 | 37.0 | 37.5 | 38.0 | 38.6 | 39.1 | 39.6 |
| 58.5 | 53.2 | 29.3 | 29.8 | 30.3 | 30.9 | 31.4 | 31.9 | 32.5 | 33.0 | 33.5 | 34.1 | 34.6 | 35.1 | 35.7 | 36.2 | 36.7 | 37.3 | 37.8 | 38.3 | 38.9 | 39.4 | 39.9 |
| 59.0 | 53.6 | 29.5 | 30.0 | 30.6 | 31.1 | 31.6 | 32.2 | 32.7 | 33.2 | 33.8 | 34.3 | 34.8 | 35.4 | 35.9 | 36.4 | 37.0 | 37.5 | 38.1 | 38.6 | 39.1 | 39.7 | 40.2 |
| 59.5 | 54.0 | 29.7 | 30.2 | 30.8 | 31.3 | 31.8 | 32.4 | 32.9 | 33.5 | 34.0 | 34.5 | 35.1 | 35.6 | 36.2 | 36.7 | 37.2 | 37.8 | 38.3 | 38.9 | 39.4 | 39.9 | 40.5 |
| 60.0 | 54.3 | 29.9 | 30.4 | 30.9 | 31.5 | 32.1 | 32.6 | 33.2 | 33.7 | 34.2 | 34.8 | 35.3 | 35.9 | 36.4 | 37.0 | 37.5 | 38.0 | 38.6 | 39.1 | 39.7 | 40.2 | 40.8 |
| 60.5 | 54.7 | 30.1 | 30.6 | 31.2 | 31.7 | 32.3 | 32.8 | 33.4 | 33.9 | 34.5 | 35.0 | 35.6 | 36.1 | 36.7 | 37.2 | 37.8 | 38.3 | 38.9 | 39.4 | 40.0 | 40.5 | 41.0 |
| 61.0 | 55.1 | 30.3 | 30.9 | 31.4 | 32.0 | 32.5 | 33.1 | 33.6 | 34.2 | 34.7 | 35.3 | 35.8 | 36.4 | 36.9 | 37.5 | 38.0 | 38.6 | 39.1 | 39.7 | 40.2 | 40.8 | 41.3 |
| 61.5 | 55.5 | 30.5 | 31.1 | 31.6 | 32.2 | 32.7 | 33.3 | 33.8 | 34.4 | 35.0 | 35.5 | 36.1 | 36.6 | 37.2 | 37.7 | 38.3 | 38.8 | 39.4 | 39.9 | 40.5 | 41.1 | 41.6 |
| 62.0 | 55.8 | 30.7 | 31.3 | 31.8 | 32.4 | 33.0 | 33.5 | 34.1 | 34.6 | 35.2 | 35.7 | 36.3 | 36.9 | 37.4 | 38.0 | 38.5 | 39.1 | 39.7 | 40.2 | 40.8 | 41.3 | 41.9 |
| 62.5 | 56.2 | 30.9 | 31.5 | 32.0 | 32.6 | 33.2 | 33.7 | 34.3 | 34.9 | 35.4 | 36.0 | 36.5 | 37.1 | 37.7 | 38.2 | 38.8 | 39.4 | 39.9 | 40.5 | 41.0 | 41.6 | 42.2 |
| 63.0 | 56.6 | 31.1 | 31.7 | 32.3 | 32.8 | 33.4 | 34.0 | 34.5 | 35.1 | 35.7 | 36.2 | 36.8 | 37.4 | 37.9 | 38.5 | 39.1 | 39.6 | 40.2 | 40.7 | 41.3 | 41.9 | 42.4 |
| 63.5 | 57.0 | 31.3 | 31.9 | 32.5 | 33.0 | 33.6 | 34.2 | 34.8 | 35.3 | 35.9 | 36.5 | 37.0 | 37.6 | 38.2 | 38.7 | 39.3 | 39.9 | 40.5 | 41.0 | 41.6 | 42.2 | 42.7 |
| 64.0 | 57.3 | 31.5 | 32.1 | 32.7 | 33.3 | 33.8 | 34.4 | 35.0 | 35.6 | 36.1 | 36.7 | 37.3 | 37.8 | 38 4 | 39.0 | 39.6 | 40.1 | 40.7 | 41.3 | 41.9 | 42.4 | 43.0 |
| 64.5 | 57.7 | 31.8 | 32.3 | 32.9 | 33.5 | 34.1 | 34.6 | 35.2 | 35.8 | 36.4 | 36.9 | 37.5 | 38.1 | 38.7 | 39.2 | 39.8 | 40.4 | 41.0 | 41.5 | 42.1 | 42.7 | 43.2 |
| 65.0 | 58.1 | 32.0 | 32.5 | 33.1 | 33.7 | 34.3 | 34.9 | 35.4 | 36.0 | 36.6 | 37.2 | 37.8 | 38.3 | 38.9 | 39.5 | 40.1 | 40.7 | 41.2 | 41.8 | 42.4 | 43.0 | 43.6 |

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## Hemlock Bark Extract.

| Degree Twaddell | Per cent. Total Solids | Purity, per cent. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 |
| | | Per cent. tannin | | | | | | | | |
| 36.0 | 40.3 | 20.1 | 20.5 | 21.0 | 21.4 | 21.8 | 22.2 | 22.6 | 23.0 | 23.4 |
| 36.5 | 40.7 | 20.4 | 20.8 | 21.2 | 21.6 | 22.0 | 22.4 | 22.8 | 23.2 | 23.6 |
| 37.0 | 41.2 | 20.6 | 21.0 | 21.4 | 21.8 | 22.3 | 22.7 | 23.1 | 23.5 | 23.9 |
| 37.5 | 41.7 | 20.8 | 21.2 | 21.7 | 22.0 | 22.5 | 22.9 | 23.3 | 23.7 | 24.2 |
| 38.0 | 42.1 | 21.1 | 21.5 | 21.9 | 22.3 | 22.7 | 23.2 | 23.6 | 24.0 | 24.4 |
| 38.5 | 42.6 | 21.3 | 21.7 | 22.1 | 22.6 | 23.0 | 23.4 | 23.8 | 24.3 | 24.7 |
| 39.0 | 43.0 | 21.5 | 21.9 | 22.4 | 22.8 | 23.2 | 23.7 | 24.1 | 24.5 | 25.0 |
| 39.5 | 43.5 | 21.7 | 22.2 | 22.6 | 23.0 | 23.5 | 23 9 | 24.3 | 24.8 | 25.2 |
| 40.0 | 43.9 | 22.0 | 22.4 | 22.9 | 23.3 | 23.7 | 24.2 | 24.6 | 25.0 | 25.5 |
| 40.5 | 44.4 | 22.2 | 22.6 | 23.1 | 23.5 | 24.0 | 24.4 | 24.9 | 25.3 | 25.7 |
| 41.0 | 44.9 | 22.4 | 22.9 | 23.3 | 23.8 | 24.2 | 24.7 | 25.1 | 25.6 | 26.0 |
| 41.5 | 45.3 | 22.7 | 23.1 | 23.6 | 24.0 | 24.5 | 24.9 | 25.4 | 25.8 | 26.3 |
| 42.0 | 45.8 | 22.9 | 23.3 | 23.8 | 24.3 | 24.7 | 25.2 | 25.6 | 26.1 | 26.5 |
| 42.5 | 46.2 | 23.1 | 23.6 | 24.0 | 24.5 | 25.0 | 25.4 | 25.9 | 26.3 | 26.8 |
| 43.0 | 46.7 | 23.3 | 23.8 | 24.3 | 24.7 | 25.2 | 25.7 | 26.1 | 26.6 | 27.1 |
| 43.5 | 47.1 | 23.6 | 24.0 | 24.5 | 25.0 | 25.5 | 25.9 | 26.4 | 26.9 | 27.3 |
| 44.0 | 47.6 | 23.8 | 24.3 | 24.7 | 25.2 | 25.7 | 26.2 | 26.7 | 27.1 | 27.6 |
| 44.5 | 48.0 | 24.0 | 24.5 | 25.0 | 25.5 | 26.0 | 26.4 | 26.9 | 27.4 | 27.9 |
| 45.0 | 48.5 | 24.3 | 24.7 | 25.2 | 25.7 | 26.2 | 26.7 | 27.2 | 27.6 | 28.1 |
| 45.5 | 49.0 | 24.5 | 25.0 | 25.5 | 25.9 | 26.4 | 26.9 | 27.4 | 27.9 | 28.4 |
| 46.0 | 49.4 | 24.7 | 25.2 | 25.7 | 26.1 | 26.7 | 27.2 | 27.7 | 28.2 | 28.7 |
| 46.5 | 49.9 | 25.0 | 25.4 | 25.9 | 26.4 | 26.9 | 27.4 | 27.9 | 28.4 | 28.9 |
| 47.0 | 50.3 | 25.2 | 25.7 | 26.2 | 26.7 | 27.2 | 27.7 | 28.2 | 28.7 | 29.2 |
| 47.5 | 50.8 | 25.4 | 25.9 | 26.4 | 26.9 | 27.4 | 27.9 | 28.4 | 29.0 | 29.5 |
| 48.0 | 51.2 | 25.6 | 26.1 | 26.6 | 27.2 | 27.7 | 28.2 | 28.7 | 29.2 | 29.7 |
| 48.5 | 51.7 | 25.9 | 26.4 | 26.9 | 27.4 | 27.9 | 28.4 | 28.9 | 29.5 | 30.0 |
| 49.0 | 52.2 | 26.1 | 26.6 | 27.1 | 27.6 | 28.2 | 28.7 | 29.2 | 29.7 | 30.3 |
| 49.5 | 52.6 | 26.3 | 26.8 | 27.4 | 27.9 | 28.4 | 28.9 | 29.5 | 30.0 | 30.5 |
| 50.0 | 53.1 | 26.5 | 27.1 | 27.6 | 28.1 | 28.7 | 29.2 | 29.7 | 30.2 | 30.8 |
| 50.5 | 53.5 | 26.8 | 27.3 | 27.8 | 28.4 | 28.9 | 29.4 | 30.0 | 30.5 | 31.0 |
| 51.0 | 54.0 | 27.0 | 27.5 | 28.1 | 28.6 | 29.2 | 29.7 | 30.2 | 30.8 | 31.3 |
| 51.5 | 53.4 | 27.2 | 27.8 | 28.3 | 28.9 | 29.4 | 29.9 | 30.5 | 31.0 | 31.6 |
| 52.0 | 54.9 | 27.4 | 28.0 | 28.5 | 29.1 | 29.6 | 30.2 | 30.7 | 31.3 | 31.8 |
| 52.5 | 55.3 | 27.7 | 28.2 | 28.8 | 29.3 | 29.9 | 30.4 | 31.0 | 31.5 | 32.1 |
| 53.0 | 55.8 | 27.9 | 28.5 | 29.0 | 29.6 | 30.1 | 30.7 | 31.3 | 31.8 | 32.4 |

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It may be said, that a slight difference exists in the tables for chestnut wood from different sections of the country and even for extracts made by different processes.

Such tables as published below are—as far as known to the writer—in use in most plants, so that it may seem useless to publish them. But to the chemist connected with one or the other of the newer extract plants it should be of benefit, giving him a foundation upon which to work.

It is the custom in reporting extracts to state the specific gravity. The tables should be accurate enough to enable the trade chemist to get from the per cent. total solids of a certain extract the corresponding degrees Twaddell, thus saving him the time of making a separate specific gravity determination.

Laboratory of Cherry River Extract Co.,
Richwood, W. Va.

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## THE WEAR RESISTANCE OF SOLE LEATHERS.*

*By Lloyd Balderston.*

Nothing which can be asked in regard to a piece of sole leather is so vital as the question "How long will it wear?" In answer to this, an expert may give a more or less correct opinion. If the opinion is based on wide experience, on knowledge of how that particular piece of leather was made, on analysis and water penetration test, besides a careful examination, it may be a sound opinion, if the expert is really expert. Any report which the laboratory can make on a sample of leather is of little value as a basis for opinion on the question of wear unless it is supplemented by all the other factors mentioned, and by still others if such can be had. If a method can be found by which the rate of wear of sole leathers in actual service can be compared, there is no doubt that it will add a very valuable item to the laboratory's report on a leather sample.

What conditions must such a test fulfil? 1. It must subject the sample to measured amounts of pressure and friction. 2. The surface against which the leather wears must be only moderately

* Read at the 13th Annual Meeting of the A. L. C. A., Atlantic City, June 2, 1916.

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rough and of such a character that it can be duplicated. 3. The rate of wear must be slow enough to avoid heating the sample. 4. The test must be so long continued that the amount worn off shall be a considerable part of the total weight of the sample. 5. There must be some accurate method of finding how much loss the sample has suffered.

These five conditions are given on the assumption that a dry test only is to be made, and that only one kind of surface is to be used. In order for a wear test to be at all complete, it should include several kinds of surfaces, both wet and dry. The method which I shall describe was designed to fulfil the five conditions. The apparatus may operate with wet or dry samples, and the wearing surface may be made interchangeable.

The apparatus holds 24 samples, ¼ inch thick, ⅞ inch wide and about 1⅛ inches long, fixed on the circumference of a wheel, the outer diameter of the circle of samples being 11 inches. This wheel revolves in contact with another of the same diameter, the outside of which is made up of four hardened steel plates, the surface of which has been roughened with a suitable tool. These plates are 1 inch wide, each covering one-fourth of the circumference of a cast iron wheel, to which they are secured by screws driven from the inside and extending only part way through the steel. The wheels are mounted on shafts 18 inches long, the other ends of which carry gear wheels. The wear wheel and the wheel carrying the samples are drawn together by a spring whose tension can be adjusted from zero to 100 pounds. A counter is attached to the axle of the sample wheel.

In the first experiments the numbers of teeth on the gear wheels were in the ratio of 25 to 26, causing a slip on each sample in each revolution of about 0.03 inch. With a pressure of 50 pounds, it was found after 25,000 revolutions that the losses were very small, less than 1 per cent. of the weight of the samples. A smaller gear was put on the shaft of the wear wheel, giving a speed ratio of about 4 to 5, and a slip on each sample of about 0.15 inch.

Forty-eight samples were cut out, representing six kinds of leather, and weighed after 24 hours, and again after another day. The changes in weight due to moisture content were found to be fairly consistent. Four samples of each kind were now put on

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the machine and the others set aside. The spring was set at 40 pounds and the apparatus run for 50,000 revolutions in about 30 hours. This number of revolutions corresponds roughly to the number of steps taken with each foot in walking 50 miles and since the samples are about one-fifth the size of a heel, the pressure of 40 pounds corresponds to about 200 pounds on a heel. The samples were now taken out and placed with the check pieces for 24 hours before weighing. They were then weighed and set aside for another day and weighed again. The change in moisture content was found fairly uniform for the four test pieces of any one kind of leather, so an average was taken for each kind and this gain or loss used as a correction in estimating the wear loss of each piece of the same kind. Results are given in Table I.

TABLE I.

| Kind | No. | Original wt. grams | Worn wt. grams | Worn wt. corrected for moisture | Loss | Loss per cent. | Average loss per cent. |
|---|---|---|---|---|---|---|---|
| Unscoured oak | 1 | 4.806 | 4.329 | 4.349 | 0.457 | 9.5 | |
| | 2 | 4.557 | 4.163 | 4.183 | 0.374 | 8.2 | |
| | 3 | 4.918 | 4.325 | 4.345 | 0.573 | 11.7 | |
| | 4 | 4.500 | 4.161 | 4.181 | 0.319 | 7.2 | 9.1 |
| Union | 1 | 4.359 | 4.012 | 4.024 | 0.335 | 7.7 | |
| | 2 | 4.395 | 4.022 | 4.034 | 0.351 | 8.0 | |
| | 3 | 4.413 | 3.955 | 3.978 | 0.436 | 9.9 | |
| | 4 | 4.151 | 3.826 | 3.848 | 0.303 | 7.3 | 8.2 |
| Hemlock | 1 | 4.617 | 4.138 | 4.108 | 0.509 | 11.0 | |
| | 2 | 4.814 | 4.303 | 4.273 | 0.541 | 11.3 | |
| | 3 | 4.800 | 4.211 | 4.181 | 0.619 | 13.0 | |
| | 4 | 4.815 | 4.321 | 4.291 | 0.524 | 10.9 | 11.5 |
| California oak | 1 | 4.164 | 3.756 | 3.736 | 0.428 | 10.3 | |
| | 2 | 3.465 | 3.220 | 3.217 | 0.248 | 7.3 | |
| | 3 | 3.399 | 3.017 | 3.006 | 0.393 | 11.6 | |
| | 4 | 3.733 | 3.226 | 3.206 | 0.527 | 14.2 | 10.8 |
| Scoured oak | 1 | 4.458 | 4.040 | 4.017 | 0.441 | 9.9 | |
| | 2 | 4.255 | 3.923 | 3.900 | 0.355 | 8.4 | |
| | 3 | 4.383 | 4.030 | 4.007 | 0.376 | 8.6 | |
| | 4 | 4.199 | 3.901 | 3.878 | 0.321 | 7.7 | 8.6 |
| Straight chrome | 1 | 3.307 | 3.076 | 3.098 | 0.209 | 6.3 | |
| | 2 | 3.031 | 2.861 | 2.883 | 0.148 | 4.9 | |
| | 3 | 3.346 | 3.112 | 3.134 | 0.212 | 6.3 | |
| | 4 | 3.310 | 3.104 | 3.126 | 0.184 | 5.6 | 5.8 |

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Excepting the California oak, the samples used in this experiment were obtained by cutting up a piece from the kidney region. No attention was paid to direction of wear, and it was thought that this might account for some of the difference shown between pieces of the same kind. In the next experiment, therefore, each piece was marked to indicate direction. A number of samples were cut from a piece taken from the kidney region of a rough oak-tanned belting butt. As these were placed in the apparatus, the direction of wear on each was noted. Four pieces of scoured oak sole leather and two of a much advertised leather substitute were included. The method was the same as before except that the pieces were weighed only once before being put in. Pieces which were more than ¼ inch thick were pared down. The pieces of chrome leather in the first experiment were less than ¼ inch thick, and they were backed with a piece of the same material to bring them to the correct thickness.

It is difficult to arrive at any satisfactory conclusion in regard to the allowance to be made for change in moisture content. In weighing the pieces on successive days, it was found that the worn pieces changed more than the unworn check pieces. This appears to be due to the more rapid absorption or evaporation through worn surfaces than through the grain of the leather. It is proposed to meet this in future experiments by putting the pieces in an air-tight vessel for several days, so that they may come to a really uniform condition. When they are exposed to the air, atmospheric changes may cause loss one day and gain the next, and the difference in the behavior of the worn and unworn pieces makes it impossible to be sure that the two are in the same condition as to moisture. Weighing both worn pieces and check pieces at the same time and computing the loss and then repeating the process the next day gives two sets of results, differing sometimes by as much as 15 milligrams in the amount of loss. In the tables I have simply given the best average I could make.

It is a debatable question how the results ought to be expressed. To take the weight worn off from a piece of a certain size is unfair to the leather whose specific gravity is high. Thus the chrome in Table I lost less than 0.2 gram per sample on the average, while the hemlock lost nearly three times as much. The

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percentage loss of the hemlock is, however, only twice that of the chrome, because of its higher specific gravity. If it were possible to estimate the relative thickness of leather resulting from tanning a hide by the two processes, we might introduce a correction on that account. Thus if the percentage loss of chrome is 6 and that of hemlock 12, on the basis of 0.25 inch thickness, while the same hide which makes ¼ inch leather by the hemlock process only makes 1/6 inch by the chrome process, the real comparison would not be 2 to 1 but 4 to 3.

Results of the second set of tests are given in Table II.

TABLE II.

(H denotes head foremost; T, tail; B, back, and Be, belly foremost.)

| Kind | No. | Original wt. grams | Worn wt. grams | Worn wt. corrected for moisture | Loss | Loss per cent. | Average loss per cent. |
|---|---|---|---|---|---|---|---|
| Rough oak belting butt | T1 | 3.691 | 3.406 | 3.369 | 0.322 | 8.7 | |
| | T2 | 3.522 | 3.232 | 3.195 | 0.327 | 9.3 | |
| | T3 | 3.604 | 3.321 | 3.284 | 0.320 | 8.9 | |
| | T4 | 3.735 | 3.432 | 3.395 | 0.340 | 9.1 | 9.0 |
| | H1 | 3.616 | 3.328 | 3.291 | 0.325 | 9.0 | |
| | H2 | 3.640 | 3.388 | 3.351 | 0.289 | 7.9 | |
| | H3 | 3.699 | 3.436 | 3.399 | 0.300 | 8.1 | 8.3 |
| | B1 | 3.774 | 3.447 | 3.410 | 0.364 | 9.7 | |
| | B2 | 3.784 | 3.502 | 3.465 | 0.319 | 8.4 | |
| | B3 | 3.628 | 3.371 | 3.334 | 0.294 | 8.1 | |
| | B4 | 3.658 | 3.401 | 3.364 | 0.294 | 8.0 | |
| | B5 | 3.558 | 3.320 | 3.283 | 0.275 | 7.7 | 8.4 |
| | Be1 | 3.456 | 3.230 | 3.193 | 0.263 | 7.6 | |
| | Be2 | 3.681 | 3.396 | 3.359 | 0.322 | 8.7 | |
| | Be3 | 3.725 | 3.432 | 3.395 | 0.330 | 8.9 | |
| | Be4 | 3.547 | 3.335 | 3.298 | 0.249 | 7.0 | 8.1 |
| Scoured oak | 1 | 4.461 | 3.928 | 3.902 | 0.559 | 12.5 | |
| | 2 | 4.379 | 3.925 | 3.899 | 0.480 | 10.9 | |
| | 3 | 4.233 | 3.750 | 3.724 | 0.509 | 12.0 | |
| | 4 | 4.303 | 3.837 | 3.811 | 0.492 | 11.4 | 11.7 |
| Leather substitute | 1 | 5.169 | 3.837 | 3.837 | 1.332 | 25.8 | |
| | 2 | 5.291 | 3.928 | 3.928 | 1.363 | 25.8 | 25.8 |

It is impossible to draw any conclusions from these figures in regard to the effect of direction on wear. The average of the tail-foremost pieces is 9 per cent., of the head-foremost 8.3 per

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cent., of the back-foremost 8.4 per cent. and of the belly-foremost 8.1 per cent. Differences among these averages are not greater than those occurring in individual sets. A rather interesting result is to be noted in regard to the leather substitute. The piece from which the samples were cut is stamped with the legend which you have all seen in the advertisements, "better than leather." These results, showing three times as much loss as rough oak belting leather, do not confirm the legend. A wet test would no doubt give a quite different set of figures. It is rather interesting also to note that rough oak belting butt wears as well as finished oak sole, either scoured or unscoured.

No claim is made that these results are in any sense conclusive, or even that the apparatus is likely to prove satisfactory. I have given this preliminary report in the hope that other members of the Association may be led to do some work on the subject, if they have not already done so, and that we may eventually arrive at a standard form of apparatus which will give dependable results.

Elk Tanning Co. Laboratory,
Ridgway, Pa.

## Discussion.

C. R. Oberfell: I think that any mechanical device which would accurately show the wearing quality of sole leather would be a very desirable thing, and Dr. Balderston has, perhaps, made an experimental step in the right direction. Also, I should think there are some tanners here who are very much interested in this matter. A few years ago the leather laboratory in charge of Mr. Veitch made some tests, not with a machine, but actual wearing tests. They obtained samples of leather and put them out and had them made into shoes for the Boy Scouts and put them out for wearing tests. I have never heard any reports from those tests and perhaps Mr. Rogers can tell us something about the results obtained.

J. S. Rogers: The results obtained in the actual wearing tests with sandals varied so greatly among themselves that we can as yet draw no conclusions from them. The personal element enters very largely into tests of this kind. The sandals were distributed among about a hundred Boy Scouts, who were given specific

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directions as to the record that should be kept of the time worn, distance covered, weather conditions—rainy or dry, whether worn on wet or dry ground, on pavements, indoors or outdoors.

The Leather and Paper Laboratory has also been working for over two years on a machine which we hope will eventually give a satisfactory wearing test on leather. It is hoped that when results are obtained with the machine the wearing tests can be interpreted. They are being held until the machine is completed.

We have not considered wearing the leather by means of a definite wearing surface of metal, for the very evident reason that any abrasive surface of metal will gradually become dulled during wear, so that at the end of any series of tests the wearing surface will not be the same as in the beginning.

One form of the machine with which we have been working has a flat revolving metal table, upon which is uniformly distributed a finely ground quartz sand, sifted to uniform size. The leather is attached to a revolving drum, and each time this revolves there is a bending action on the leather as it comes in contact with the wearing surface. The speed at which the revolving drum travels is different from that of the plate on which it runs so that there is a slight rubbing or slipping motion of the leather against the sanded plate. The object is to imitate as closely as practicable the wear and motions of walking.

There are, of course, several different methods of measuring wear. Some of the outstanding objections to each method may be mentioned. There are objections to determining the wear by loss of weight. Perhaps the first is the variation of the moisture content of the leather, which Dr. Balderston has already mentioned. In our tests we have avoided this by weighing the samples in a "constant temperature, constant humidity room" in which the humidity is regulated to within two or three degrees above or below 65 per cent. at 70° F. The samples remain in this room at least 24 hours before each weighing. An objection to the use of sand as the wearing material is that sufficient sand may be imbedded in the leather to give an increase in weight. This error might be corrected by making ash determinations on the leather before and after wear, but this may not be practicable, because the variation in ash in different parts of the hide is greater than one would suppose.

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In determining the wear by measuring the decrease in thickness, it is found that the wear is not uniform over the piece of leather, and the average of 20 measurements over a piece of leather 3 x 7.25 inches, although fairly good, is not always reliable and so this method may not be satisfactory. Another difficulty in measuring wear by the decrease in thickness is that the thickness is decreased by compression, as well as by actual wear.

At present we are working on a device for measuring the total volume of the leather before and after wear. Displacement methods using water or any liquid which will wet the leather of course cannot be used. Mercury promises to be suitable for the purpose.

The results obtained by Dr. Balderston are interesting and though the problem is not a simple one it is believed that in the near future a machine by means of which the comparative wearing quality of sole leathers may be very satisfactorily determined will be developed.

The Leather and Paper Laboratory of the Bureau of Chemistry has been actively engaged in this work for some time and will appreciate co-operation of the tanners and shoe manufacturers, both in suggestions and materials for experiment.

ALLEN ROGERS: I was very much interested in Dr. Balderston's results. They confirm some tests we made about five years ago, comparing chrome tanned with vegetable tanned leather. The test was conducted with twenty mail carriers and twenty policemen. Chrome leather was used on the right foot, and the best oak sole on the left foot. In practically all cases the mail carriers and the policemen wore out two oak soles and were on the third when the chrome went through, which is practically the same as the results Dr. Balderston reached, with the chrome running twice as long as the oak leather. Thus the laboratory tests check up pretty well with the actual wearing tests. We used Swiss hides—very heavy hides, weighing about 90 pounds each.

J. H. YOCUM: May I ask the doctor whether the oak soles he speaks of were purchased or were they tanned from the Swiss hides?

A. ROGERS: No, these oak soles were all put on by one cobbler

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who claimed to have a fine oak sole. I cannot say what they were.

J. H. YOCUM: How was the thickness?

A. ROGERS: They were of the same thickness. I cannot say much about the vegetable tan, excepting that the cobbler from whom they were bought claimed it was the finest oak sole he could get.

J. H. YOCUM: In renewing the soles was the same leather used?

A. ROGERS: Yes, the same cobbler did all the work.

J. H. YOCUM: In 1875 a committee who were getting up specifications for the issuance of prizes and medals in Philadelphia sent out a notice to sole leather tanners that they were going to make tests on the wearing qualities of different leathers and determine their values as made clear by these tests. A sole leather tanner who was then tanning India buffaloes, acid hemlock leather, proceeded to purchase about a dozen of the heaviest bulls he could buy in Chicago. He tanned them for nine months and sent them on; a most homely piece of leather—I don't remember it myself—but such was the report. The test was to put a given size piece of leather—measuring it up, getting a certain proportion to the square inch—against the grinding surface of a grindstone, and this tanner received the gold medal.

Different kinds of hides will give different wearing tests, as well as different parts of the same hide, and it seems to me useless to expect to get concordance in these tests unless one takes the leathers from the same kind of hide and from the same part of the hide. For instance, Texas will furnish you a more permanent sole than will a native. If you go out and buy bloom oak leather you will naturally get Texas; if you go out and buy scoured oak leather, you will get a native or a Colorado. It seems to me that the variation in the hides, and the place from which the leather is cut, has so much to do with the results that it is utterly impossible for any tests or measurements to be of any value so far as showing the wearing quality of sole leather.

A. H. LOCKWOOD: It seems to me that before you get very far in this direction you will have to consult the shoe manufacturer. The peculiar wear on a shoe is something that is very difficult to analyze. It is a combination of twisting, torsion, etc. The thing

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is well illustrated by the linen thread that is used to attach the soles to the uppers. This linen thread has a breaking strength of 100 pounds. If you multiply the number of threads by which the sole is attached to the upper, you will find they are fastened together by a tensile strength of several tons. Of course, this does not presuppose that some terrific force is going to grasp the upper and the sole and try to tear them apart, but these threads sometimes break. It is the twisting, torsional strain. You can take a half dozen men and give them the same shoes, and you will find that one man will wear them out in one month, another in six months, and they may last the third man a year.

I think it would be impossible to get any machine which would approximately imitate the peculiar wear to which leather is subjected in a shoe.

Another important thing that should be taken into consideration is the acid excretions from the feet. One person will get a pair of shoes, and the acid excretions from his feet will almost dissolve the leather in a few days. Another person might wear them indefinitely. I think we are going into a question which it is exceedingly difficult to reduce to a scientific basis.

J. H. YOCUM: I would like to ask the doctor if he made any attempt to compare the loss in weight with relation to the kinds of leather used.

L. BALDERSTON: I did not make any definite comparison of that sort, but the fact, for instance, that the specific gravity of the hemlock sole I was using was very much higher than that of the oak sole or the chrome leathers that were being used was the reason I put my results in percentage form. The percentage losses come as near getting a relative statement of the loss as anything I can think of.

J. H. YOCUM: May I ask, Doctor, which side of the leather you used for the friction test?

L. BALDERSTON: The grain side against the wheel.

J. H. YOCUM: You used some acid leather?

L. BALDERSTON: Yes.

J. H. YOCUM: Some scoured oak?

L. BALDERSTON: Yes.

J. H. YOCUM: How much difference in the thickness was there in the grain?

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L. BALDERSTON: I don't know. I didn't measure the thickness of the grain.

J. H. YOCUM: I think if you could get a bearing on this loss in relation to the kinds of leather, and get down to the loss as compared with the hide substance in the leather, it might show something of value.

C. R. OBERFELL: I take it that Dr. Balderston's work was preliminary and that he has not been able to carry it to that point as yet.

S. SAXE: I would like to ask Mr. Balderston, if he was having a pair of shoes made, which leather he would give the preferance to?

L. BALDERSTON: I am not ready to answer that question—not so ready as I was before I tried these experiments.

W. H. DICKERSON: It has just occurred to me that in some of the mining regions, the miners insist on having the flesh side of the sole leather out. They claim that the leather will pick up, in the flesh side, grit, etc., which will be held there and increase the wearing qualities of the sole very greatly.

C. R. OBERFELL: That is a phase I have never heard brought up before. Mr. Yocum, do you know anything about the wearing qualities of leather on the grain side as compared with the flesh side?

J. H. YOCUM: It is true that the flesh side will wear longer if put out than the grain side. The film that lies between the flesh side is more resistant to wear than is the grain. The grain is put on the outside of shoes because of the appearance, not because of its wearing qualities.

A. ROGERS: Another point may be mentioned in reference to wearing chrome soles. You will notice they are all soft—like rubber almost, while an ordinary sole is smooth. I wonder, therefore, if the chrome sole would not add a little to the wearing because it is more or less yielding, and possibly it fills up with dirt and grit as Mr. Dickerson mentions.

One of the objections to chrome leather for a person whose feet perspire is that it does not absorb the moisture.

F. A. LOVELAND: For some years we have been tanning both chrome and vegetable leather made from the same class of hides. For the last two years we have been making both hard and soft

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chrome, flexible chrome, made with the idea of taking the place of rubber soles which were coming into the market so freely about two years ago. We find the flexible chrome will wear about the same length of time as the hard sole and in both cases we find that the wear is about twice as long as the vegetable sole made from the same class of hides. We found also that the chrome sole leather made from the same class of hide is not quite so thick as that made by the acid process.

C. R. OBERFELL: How were your tests made? In what way?

F. A. LOVELAND: By putting on rights and lefts.

V. A. WALLIN: I have had no experience in testing the wear of soles, but a point came up last year in reference to chrome tanned and wax-filled leathers, that where a sole is heavily wax-filled, whether chrome or vegetable tanned, and the shoes are worn in the winter time, in every place, in different cases, where the shoes have been introduced, there has been a lot of complaint about cold feet.

It was a surprise to me. I had an idea if you had a wax-filled sole that your feet would be warmer and drier, but the exact opposite is true,—that a heavy, dense shoe is a splendid conductor of cold. The men who wore the shoes also complained that their feet were wet. It was not that their feet had gathered the moisture through the sole, but that the cold had struck through the sole, and the moisture of the perspiration gave them wet feet.

C. C. SMOOT: I have never made any actual tests, except some wearing tests on shoes. We made some chrome soles some years ago in an experimental way and we tried it out and found the chrome sole outwore the other, particularly where it was filled with wax.

I think in the case referred to by Mr. Wallin the feet got cold simply because the leather did not absorb the moisture exuded by the feet.

C. R. OBERFELL: Efforts of the kind which Dr. Balderston has made are very interesting and are of decided value, even if they do not yield positive results. If we know what is impossible, it is sometimes as valuable as to know what is possible. It saves some other investigator just that much work, and these investigations become a permanent record in the JOURNAL of the A. L. C. A. where they may be readily consulted.

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# THE ACTIVATED-SLUDGE PROCESS IN TREATMENT OF TANNERY WASTES.*

*By Harrison P. Eddy and Almon L. Fales,*
Of Metcalf & Eddy, Consulting Engineers, Boston and Chicago.

## General Treatment of Industrial Wastes.

The activated-sludge process of sewage treatment may be particularly well adapted for the treatment of some industrial wastes. The firm with which the writers are connected is now directing activated sludge tests on paper-mill wastes at the mills of Bird & Son, East Walpole, Mass., on woolen-mill wastes at the Assabet Mills of the American Woolen Co., Maynard, Mass., and on tannery wastes at the factories of Winslow Bros. & Smith Co., Norwood, Mass. The tests on woolen-mill wastes have not been conducted for a sufficient length of time to afford any indication as to the practicability of treating these wastes by the activated-sludge process. The tests on the paper-mill wastes are not very encouraging, although various modifications of the process, which are being tried on an experimental scale, may solve the problem. The results of the tests on the tannery wastes are very promising, although it remains to be determined whether the method will be economical. A brief account of the activated-sludge tests made thus far on these tannery wastes may prove of interest.

## Character of Wastes.

The Winslow Bros. & Smith Co. manufacture sheep, calf, and kid leather and pulled wools. The wool-scouring liquors, amounting to about 30,000 gallons a day, are degreased by the acid-cracking process and a large part of the grease is subsequently recovered. The combined wastes from the tannery and degreasing plant average about 500,000 gallons each working day. This does not include about 250,000 gallons a day of comparatively clean rinse waters discharged into the brook without treatment other than by fine screens.

The individual wastes from the various processes are discharged at different times and in different quantities, causing a marked variation in the character of the combined wastes. The composite for the day is gray or brown in color, densely turbid,

* *Journal Ind. and Eng. Chemistry*, July, 1916, pp. 648-651.

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and malodorous. It contains much suspended matter, but after settling remains densely turbid. Tests showed that for each 100 parts by weight of solids settling in 24 hours, there were 63 parts of non-settling suspended and colloidal matter. The combined wastes are frequently acid in nature, due to the discharge of certain acid wastes, but the daily composite is generally alkaline.

TABLE I.—TESTS OF COMBINED FACTORY WASTES AND ACTIVATED-SLUDGE TANK EXPERIMENTS AT FACTORY OF WINSLOW BROS. & SMITH CO.

Results in Parts per Million (Except last column).

| | (A)—Factory wastes | | | (B)—Activated sludge | | |
|---|---|---|---|---|---|---|
| | Average for | Monthly average | | Tank tests (a) | | Decrease Per |
| Determinations | 1915 | Max. | Min. | Influent | Effluent | cent. |
| Total oxygen consumed | 889 | 979 | 759 | 785 | 258 | 67.1 |
| Dissolved | 554 | 670 | 386 | 605 | 244 | 59.6 |
| Suspended | 335 | 427 | 259 | 180 | 14 | 92.2 |
| Total albuminoid nitrogen | 29.3 | 36.4 | 21.1 | 21.5 | 5.5 | 73.0 |
| Dissolved | 16.2 | 21.9 | 10.8 | 16.0 | 4.4 | 72.5 |
| Suspended | 13.1 | 18.7 | 9.9 | 5.5 | 1.4 | 74.6 |
| Ammonia nitrogen | 17.9 | 25.1 | 13.3 | 25.5 | 9.9 | 61.1 |
| Nitrites | .. | .. | .. | .. | 1.90 | .. |
| Nitrates | .. | .. | .. | .. | 0.06 | .. |
| Total residue | 3,915 | 4,902 | 2,882 | 3,088 | 2,356 | 23.7 |
| Loss on ignition | 1,352 | 1,862 | 1,057 | 836 | 272 | 67.3 |
| Fixed residue | 2,563 | 3,339 | 1,825 | 2,252 | 2,084 | 7.4 |
| Total dissolved solids | 2,671 | 3,560 | 1,766 | 2,726 | 2,340 | 14.1 |
| Loss on ignition | 520 | 606 | 375 | 514 | 258 | 49.8 |
| Fixed residue | 2,151 | 3,025 | 1,388 | 2,212 | 2,082 | 5.8 |
| Total suspended solids | 1,243 | 1,690 | 993 | 362 | 16 | 95.5 |
| Loss on ignition | 831 | 1,294 | 622 | 322 | 14 | 95.6 |
| Fixed residue | 412 | 674 | 248 | 40 | 2 | 95.0 |
| Total sulphur | 227 | 300 | 144 | 252 | 251 | 0.4 |
| Fats by ether extraction | 486 | 780 | 312 | 255.2 | 48.5 | 81.1 |

The average results of analyses of the crude wastes for 1915, together with the maximum and minimum monthly averages for the different constituents, are given in Table I (A). These wastes are several times as strong as ordinary domestic sewage. It was found that one volume of settled wastes required, on the average, about 50 volumes of unpolluted brook water to produce stability. These wastes have a marked avidity for oxygen, as much as 240 milligrams of oxygen per liter of wastes being absorbed immediately from water used for dilution. This would

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be enough to saturate with dissolved oxygen about 25 times this volume of distilled water at room temperature.

### Present Method of Treatment.

The combined wastes are pumped to sedimentation tanks, having a total capacity of nearly 1,000,000 gallons. Lime in the form of milk of lime is added to the crude wastes whenever necessary in sufficient amount to maintain an alkaline tank effluent. A portion of the tank effluent is applied to sand filter beds, an area of 3.5 acres being available for this treatment. The remainder is treated by dilution with water from an 800,000,000 gallon reservoir controlled by the company.

### Object of Experiments.

Sufficient diluting water is not available for complete oxidation of the tank effluent during the greater part of the year. Several times the present area of filter beds would be required to filter properly the entire volume of wastes under favorable weather conditions, and it is not practicable to keep the filter beds in working order during the winter. Moreover, the cost of operation and maintenance of the filter beds has proven excessive, principally because of the very large proportion of finely divided suspended matter and colloids in these wastes.

In order to ascertain whether the trickling filter would not be better adapted for the purification of these wastes tests on a large working scale were authorized. These tests, carried on for 18 months, indicated that by this method a satisfactory effluent could be obtained at much less cost than by the sand filter method. The principal drawbacks in this process were the danger of the dissemination of foul odors by the spraying of the liquid on the filter and possible trouble from moth flies, which are common to this type of filter. The cost of construction of a one-acre trickling filter 7.5 feet deep with dosing tank, secondary sedimentation tanks, and other equipment, capable of satisfactorily purifying all of the waste waters from the factory was estimated at $63,480.

Before the trickling filter tests were completed the activated sludge process of sewage treatment came into prominence. This process, if it could be economically applied to the treatment of

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these wastes, promised to avoid any possible fly nuisance and to reduce the foul odors to a minimum. Moreover, it was to be expected that a suitable activated sludge plant might be constructed for much less than the cost of a trickling filter plant. We were accordingly authorized by the company to conduct activated sludge tests on a working scale.

## Description of Experimental Plant.

A 1,000-gallon aeration tank approximately 6 feet long, 3 feet wide and 8 feet deep was built in one corner of the pressroom of the degreasing plant. This room is not very warm in cold weather, but the temperature is high enough to prevent freezing. The tank is provided with a complete false bottom of filtros plates (Grade 5 R), 6 inches above the true bottom, for diffusion of the air. The air space is divided into three independent longitudinal ducts to make it possible to cut out the outside ducts and by sloping the sides to the middle duct to operate with one-third of the volume of air required for agitation with the complete false bottom if it should be found that a smaller volume of air is sufficient for oxidation. The air is taken from the pipe supplying compressed air for mixing the treated wool-scouring liquors in the acid-cracking tanks, under a pressure of about 50 pounds per square inch, which is reduced to the required pressure of opproximately 3.5 pounds by a Mason pressure-reducing valve. The consumption of air is measured by a Westinghouse gas meter supplied by the Pittsburgh Meter Co.

The joints between the filtros plates were first made with Arco-Sealit roofing compound. When the liquid in the tank reached a temperature between 70° and 80° F. this material softened and the pressure of air from beneath blew holes through it. Various high-melting-point pitches and asphalts were tried, but none was found which we felt certain would not give way under the conditions of warm temperature and air pressure. The lower part of the joints was then made with one of the best pitches and the upper part was filled with rich cement mortar.

The wastes are drawn by gravity into the aeration tank, and the supernatant liquor drawn off by means of a flexible-jointed pipe. A sludge draw-off pipe is provided at the bottom of the tank. Provision is made for sampling from the influent and ef-

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fluent pipes during the filling and drawing of the tank, and four sampling outlets in the tank at different depths are available for making special tests.

### Preliminary Treatment.

In view of the constantly changing character of the wastes during the day it was considered necessary to equalize them before applying the activated-sludge treatment. It was, therefore, decided to use the effluent from the sedimentation tanks for the tests. By this preliminary treatment there is removed not only the heavy matter in the wastes, which would require an excessive amount of air to keep it in suspension, but also the other settling suspended matters, which would require large amounts of air for their oxidation. No difficulty has been experienced in dewatering the sedimentation sludge on drying beds without causing complaints from foul odors. All the dried sludge is being carried away, without expense to the company, by the farmers in the vicinity who use it as fertilizer.

### Beginning of Tests.

The aeration tank was put into operation December 29, 1915, on a schedule of one filling each working day. Air was applied at a sufficient pressure to maintain a good agitation of the tank contents, and the aeration continued for about 20 hours, when the aerated wastes were allowed to settle for a period of 2 hours, after which the supernatant liquor was drawn off and replaced with fresh sedimentation-tank effluent. The tank was not filled on Sundays, and air was applied for about 44 hours from Saturday to Monday. After 9 fillings it was found that 4.6 per cent. of sludge (based on 2 hours' sedimentation) had accumulated in the aeration tank, but the treatment was effecting no perceptible change in the liquor applied.

### Artificial Heating of Wastes.

It became apparent that it would be a very slow process, if indeed possible, to activate the sludge at the low temperature of the wastes, less than 50° F. It was therefore considered advisable to warm the tank liquor to expedite the tests. It is impracticable to do this by heating the air supplied. The specific heat

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of air is approximately 0.238 (water = 1), whence 4.2 times as much air as water by weight is required to produce a given result in heating or cooling. The specific gravity of air is 0.00129 + (water = 1), whence 1 volume of water weighs the same as 775 volumes of air. The relative volumes of air and water at a given temperature to have the same calorific power are, therefore, as 3,250 : 1. On the basis of the above computations 100 times the actual quantity of air being used for 20 hours' aeration would be required at 90° F. to raise the wastes from 50° to 70° F. in 20 hours. If the air were heated to 212° F., 500 times the quantity of air being used per hour would be required to raise the temperature of the wastes from 50° to 70° F. in 1 hour. The quickest and most economical way to heat the liquor appeared to be by live steam admitted to the tank. The application of a moderate amount of steam for 2 to 3 hours is sufficient to raise the temperature of the wastes to 70° F. The effect of live steam on the bacterial life within the filter was conjectural. It was found, however, that after less than one day's aeration at the higher temperature the dark gray liquor became reddish in color and showed partial clarification.

After carrying on the tests for 2 or 3 days at the warm temperature the pitch which had been used to form the joints between the filtros plates softened to such an extent that the air pressure blew holes through it, thus necessitating the withdrawal of the sludge and the making of new joints with cement mortar as previously described. The tank was out of use from January 10 to January 22, during which time the sludge accumulated prior to January 10 was stored in a cool place. When it was returned to the tank on January 22, it had become very foul—in odor like decaying fish. In spite of this fact, there was a decided improvement from the first in the appearance of the tank liquor on aeration at the warm temperature. The top liquor drawn January 28, was free from disagreeable odor and was only slightly turbid.

### Activation of Sludge.

By February 7 there had accumulated 20 per cent. of sludge based on a working capacity 7 feet 6 inches deep and a period of sedimentation of 2 hours. It was then decided to aerate continuously without further addition of liquor until the sludge be-

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came activated. Steam was applied from time to time with a view to maintaining a temperature between 65° and 75° F. Occasionally the temperature dropped below 60° F., but the liquor was not allowed to remain at that temperature for any considerable length of time.

The nitrite and nitrate nitrogen in the liquid being aerated gradually increased from a trace on February 8 to 3.5 parts per million on February 17. It then jumped to 12 parts per million on the following day and continued to increase, reaching about 35 parts per million on February 24, which is higher than has ever been obtained in the effluent from the sand filters. Nearly all of this was nitrite nitrogen. The continuous aeration was extended until March 6 to ascertain whether it would be possible to convert the nitrite into nitrate. This was not accomplished, presumably because the nitrate-forming organisms were absent.

On February 18, after 11 days' continuous aeration, the settled tank liquor was found to be perfectly stable. A chemical analysis of a sample collected February 25 showed 4.9 parts per million albuminoid nitrogen—a reduction of 63 per cent. from that in the influent—and 0.5 part per million of ammonia nitrogen, a reduction of 97 per cent. from that in the influent. Shortly after this the air was accidentally turned on at full pressure. This broke up the coagulant to a marked degree so that much fine suspended matter remained in the liquor after settling for 2 hours. This fine suspended matter did not coagulate again on further aeration and continued to render the tank liquor exceedingly turbid.

The continuous aeration started February 7 caused the sludge to become more granular in nature so that it tended to be more compact on standing and thus to occupy less space. Further, the continued application of air and the occasional introduction of steam tended to break up the coagulant, thus rendering the sludge resulting from sedimentation of the liquor denser and of less volume. The sludge volume of 20 per cent. on February 17 was reduced to 13 per cent. on February 25 and after the excessive application of air to only 7.6 per cent. on March 5.

### Results of Operation at One Filling a Day.

Beginning March 6, the tank was again put into operation on

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the schedule of one filling each working day. Air was applied at the rate of about 0.5 cubic foot per gallon per hour, or approximately 10 cubic feet per gallon per day, based on 20 hours' aeration. By the end of March the accumulation of sludge, based on 2 hours' sedimentation, was equivalent to 17.8 per cent. of the working capacity of the tank.

The character of the effluent of the activated-sludge tank continued to improve until it became practically clear and nearly free from suspended matter. Beginning March 16 the effluent was perfectly stable by the methylene-blue test. No considerable amount of nitrification, however, is yet taking place. The last weekly analyses of sterilized composite daily samples of influent and effluent are given in Table I (B). It will be seen that a very large proportion of the fine suspended matter and a considerable proportion of the dissolved organic matter in the influent are being removed by the activated-sludge treatment.

## Character of Activated Sludge.

The sludge from the aeration of these tannery wastes is reddish brown in color and flocculent in nature, being very similar to that resulting from the aeration of sewage. It is free from offensive odor and comparatively stable. Partial analyses of this sludge, made during March, gave the results appearing in Table II.

TABLE II.—Partial Analyses of Activated Sludge (Percentages).

| Date 1916 | Moisture | Dry solids | Composition of dry solids: Organic | Mineral | Fats |
|---|---|---|---|---|---|
| March 5 | 98.79 | 1.21 | 66.1 | 33.9 | 7.3 |
| 10 | 98.58 | 1.42 | 71.1 | 28.9 | 9.1 |
| 18 | 98.16 | 1.84 | 72.3 | 27.7 | 9.4 |
| 27 | 97.70 | 2.30 | 74.8 | 25.2 | 11.6 |

The increasing percentage of dry solids, organic matter, and fats in the accumulating sludge is worthy of note.

The analyses in Table II were made on sludge resulting from 2 hours' sedimentation. That there is a wide difference in the volume of sludge after different periods of sedimentation is shown by Table III.

TABLE III.—Volume of Activated Sludge after Different Periods of Sedimentation in Measuring Glasses.

| Sedimentation periods (hrs.) | ¼ | ½ | ¾ | 1 | 1½ | 2 | 3 | 4 | 18 |
|---|---|---|---|---|---|---|---|---|---|
| Sludge (per cent. of sample) | 25.0 | 22.0 | 20.7 | 18.6 | 16.6 | 14.7 | 13.3 | 12.8 | 11.3 |

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### Period of Sedimentation Required.

The amount of suspended matter remaining in the aeration tank liquor after different periods of aeration on April 6, 1916, gave the results noted in Table IV.

TABLE IV.—Suspended Matter (P. p. M.) in Aeration Tank Liquor after Different Periods of Sedimentation.

| Period of sedimentation (hrs.) | ¼ | ½ | 1 | 2 | 4 | 8 |
|---|---|---|---|---|---|---|
| Suspended matter in supernatant liquor | 260 | 86 | 64 | 50 | 32 | 22 |
| Reduction by sedimentation in succeeding period | | 174 | 22 | 14 | 18 | 10 |
| Reduction per hour | | 696 | 44 | 14 | 9 | 2.5 |

Though a very large proportion of the suspended matter was removed by ½ hour's sedimentation considerable fine suspended matter continued to settle after that. Undoubtedly mass action in a large tank would bring about more rapid sedimentation.

### Amount of Air Required.

Considerable trouble has been experienced from frothing due to the soapy character of the wastes aerated and caused principally by the necessity of discharging some wool-scouring liquors into the wastes channel without degreasing until certain improvements in the degreasing plant have been completed. This trouble has necessitated cutting down the air supply to the minimum which will furnish sufficient agitation. At a rate as low as 0.25 cubic foot per hour of air per gallon of wastes aerated, 20 hours' aeration was insufficient to produce stability. There are indications that double this rate of applying the air will be more economical. Even at the higher rates of application of air the aeration-tank liquors show only about 15 per cent. saturation of dissolved oxygen after 20 hours' aeration. It is hoped that the period of aeration may be materially shortened as the tests progress. The effect of an increasing proportion of activated sludge, of reduction in the temperature of aeration, and of variation in the depth of liquor aerated remain to be studied.

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# TREATMENT OF PACKING-HOUSE SEWAGE BY AERATION IN THE PRESENCE OF ACTIVATED SLUDGE.*

*By Paul Rudnick and G. L. Noble.*

Chief Chemist and Chemist, Armour & Company.

This paper is a brief account of experiments with the activated-sludge process[1] on sewage from the plant of Armour & Co., at Chicago.

An idea of the extreme variation in the nature and composition of the different kinds of sewage involved may be obtained from the following list of the more important departments where this sewage originates: Hog, beef and sheep abattoirs, power plant, lard refinery, oleomargarine, meat-canning, meat-curing and sausage departments, rendering tanks, fertilizer plant, several other smaller departments, and the domestic sewage of 10,000 employees. This sewage is much more concentrated than domestic sewage, containing approximately four times as much suspended solids. Averages of recent analyses, including analyses of night and holiday sewage, show the composition in Table I. The suspended solids consist largely of organic material. The high content of inorganic matter is caused to great extent by the deep-well water used in many departments, the total solids of which is more than 2,000 parts per million.

TABLE I.—SOLIDS IN RAW SEWAGE: PARTS PER MILLION.

| | | | |
|---|---|---|---|
| Organic | 560 | Organic suspended solids | 425 |
| Inorganic | 2,990 | Inorganic suspended solids | 75 |
| Total | 3,550 | Total suspended solids | 500 |

Sewage from each of the three main outlets is pumped into a weir box, which also acts as a small grit chamber. From this the sewage passes into an aerating tank 10 feet by 20 feet by 10 feet, where it is aerated for 10 hours. A partition is arranged so that the path of the flow is about 40 feet long. Sludge containing 99.5 per cent. water, which has been aerated for 3 hours, is

* *Journal Ind. and Eng. Chemistry*, July, 1916, pp. 651-652.

[1] G. J. Fowler, E. Ardern and W. T. Lockett, *J. Soc. Chem. Ind.*, **31**, (1912), 471; E. Ardern and W. T. Lockett, *Ibid.*, **33** (1914), 523 and **34** (1915); 937; E. Bartow and F. W. Mohlman, *Jour. Ind and Eng. Chem.*, **7** (1915), 318 and **8** (1916), 16; T. C. Hatton, *Eng. News*, **74** (1915), 134 and *Eng. Rec.*, **72** (1915), 481. Abstract this JOURNAL, **9**, 331; **10**, 647; **11**, 211-2.

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introduced into the aerating tank at the same point as the raw sewage at the rate of 30 per cent. of the raw sewage flow. The aerating tank is fitted with underflow and overflow baffles, and the air is distributed by means of $^3/_4$ inch pipes perforated with $^1/_{25}$-inch holes, 2 inches apart and staggered, the pipes being placed at 4-foot intervals at right angles to the line of flow. After leaving the aeration tank the sewage is allowed to settle 40 to 60 minutes in a separate chamber. The sludge is siphoned continuously into the sludge storage and the effluent continuously flows over the edges of the settling chamber. The air is measured by means of an orifice and differential manometer: 3 cubic feet of air are required per gallon of sewage. This includes the air used for siphoning the sludge from the settling chamber to the sludge storage and from the sludge storage to the aerating tank for inoculation. The effluent is fairly clear and practically odorless. The methylene blue test[2] shows that it is nonputrescible for at least 4 days. Typical sanitary analyses of the effluent are shown in Table II.

TABLE II.—NITROGEN CONTENT OF EFFLUENT: PARTS PER MILLION.

| Albuminoid | Ammonia | Nitrite | Nitrate |
|---|---|---|---|
| 2.40 | 23.80 | 0.60 | None |
| 7.40 | 16.20 | 0.07 | None |
| 3.00 | 31.20 | 0.25 | None |
| 4.10 | 27.90 | 0.15 | None |
| 2.50 | 28.60 | Trace | None |

The change in the composition of the sewage caused by the aeration process is concisely shown in Table III, which gives the percentage of decrease of certain constituents.

TABLE III.—APPROXIMATE PERCENTAGE REDUCTION OF CERTAIN CONSTITUENTS BY AERATION.

| Albuminoid nitrogen | Ammonia nitrogen | Total organic nitrogen | Total organic matter | Suspended solids |
|---|---|---|---|---|
| 96 | 71 | 66 | 70 | 95 |

A very important factor in the decomposition of the sludge is its high content of moisture and the difficulty of dewatering it in large quantities. A summary of a series of analyses of sludge obtained from the experimental unit is given in Table IV,

[2] Am. Pub. Health Assoc., "Standard Methods for the Examination of Water and Sewage," 2nd Ed., 1912, 63.

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which shows also the limits which may be expected for the fertilizer value and the fat content of the dried sludge.

TABLE IV.—ANALYSES OF SLUDGE: RESULTS IN PERCENTAGES.

| | Moisture | Ammonia (*a*) | Nitrogen (*a*) | Fat (*a*) |
|---|---|---|---|---|
| Number of analyses | 12 | 18 | 18 | 17 |
| Maximum | 99.70 | 7.84 | 6.46 | 9.36 |
| Minimum | 99.10 | 3.60 | 2.96 | 1.98 |
| Average | 99.48 | 5.57 | 4.59 | 5.54 |

(*a*) Calculated to a commercially dry (10 per cent. moisture) basis.

The dry sludge contains very small proportions of phosphoric acid (approximately 2 per cent. calculated as $P_2O_5$) and potash (approximately 0.4 per cent. calculated as $K_2O$) and its fertilizer value therefore lies entirely in its content of nitrogen.

Much work has been done to find some practicable means of dewatering the sludge so that it may be obtained in a form in which it can be dried in the driers regularly used for handling fertilizer materials. The moisture content of the wet sludge coming from the settling chamber must be reduced from 99.5 to 50 per cent. if possible. The importance of this problem is brought out much more clearly when it is considered that such reduction involves the removal of almost 99 per cent. of the weight of the wet sludge as it comes from the settling chamber.

Filter pressing in the ordinary type of filter press and in the newer forms, such as Kelly or Sweetland presses, has proved entirely unsuccessful. The filter cloths are very rapidly clogged. A special type of filter press may be developed for this purpose and experiments in that direction are under way. Centrifuges of the imperforate-bowl type have also been tried, but it will be difficult to construct a machine of sufficient capacity to bring the cost of installation to a nonprohibitive amount. After the sludge has been reduced to a 50 per cent. moisture content it can be readily and cheaply dried in the usual driers employed for drying organic ammoniates for fertilizers. As available space is an important consideration, an investigation into the possible depth of aerating tanks was made. Two pipes 14 inches in diameter were erected, one 36 feet and the other 18 feet high. The air, which was discharged through perforated pipes, was allowed to pass into each unit in equal amounts. The sewage used for this experiment came from the beef abattoir. Samples

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were taken at regular hours covering several days and the albuminoid, ammonia, nitrite and nitrate nitrogens, and the putrescibility were determined. As the results in either pipe were practically identical it was concluded that an aerating tank of any depth to 36 feet will produce as good results as a more shallow tank in respect to purification of sewage. Economy in consumption of air should also be considered in this connection.

The bacteriological data are too meagre to warrant conclusions, but two facts are apparent: (1) 3 or 4 hours' aeration of the sludge from the settling chamber increases the number of organisms, but further aeration reduces them somewhat; (2) the organisms grow better at 20° than at 37° C. as might be expected. Throughout the records there seems to be a correlation between warm sewage temperatures above 75° F. and inactivity of the organisms, which results in an inactive sludge. This may be an obstacle that will prevent the placing of a disposal plant close to the abattoir where the sewage temperature may suddenly change from cold to hot or *vice versa*.

The results of the experimental work warrant the belief that this process offers more promising possibilities than any of the other methods of disposing of packing-house wastes hitherto proposed. The relatively small area required for installation, the comparatively high nitrogen content of the sludge, the comparative clarity and stability of the effluent, and the relatively short time of treatment are perhaps the most important features of the process.

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# SODIUM SULPHATE AS A SUBSTITUTE FOR POTASSIUM SULPHATE IN THE GUNNING MODIFICATIONS FOR DETERMINING NITROGEN.*

*By W. L. Latshaw.*

Owing to the extremely high price of potassium sulphate, chemists who favor the Gunning modification of the Kjeldahl method for determining nitrogen are looking for a cheaper substitute to take the place of the more expensive potassium sulphate. Quotations recently received at this laboratory from several firms range in price from $1.25 to $2.25 per pound for the powdered chemical suitable for use in nitrogen work, while quotations on suitable sodium sulphate were only 15 cents per pound. Because of the similarity in chemical characteristics between potassium sulphate and sodium sulphate, a series of determinations was made to compare the use of these two salts in making nitrogen determinations.

In the first trials, where 10 grams of the water-free salts were used in comparison, both worked very nicely during digestion, but on cooling, the digest in which sodium sulphate was used caked into a solid mass, and as this was objectionable 7 to 8 grams of sodium sulphate were used with the results shown in Table I.

TABLE I.

(RESULTS IN PERCENTAGES.)

| | The Gunning copper method substituting sodium sulphate | | | | The official Gunning copper method | | | |
|---|---|---|---|---|---|---|---|---|
| Substances | No. of dets. | Max. | Min. | Av. | No. of dets. | Max. | Min. | Av. |
| Dried blood .. | 3 | 14.97 | 14.93 | 14.95 | 3 | 14.96 | 14.92 | 14.95 |
| Casein ..... | 3 | 12.72 | 12.68 | 12.70 | 3 | 12.71 | 12.67 | 12.69 |
| Milk albumin | 6 | 9.07 | 8.89 | 8.99 | 3 | 9.00 | 8.96 | 8.98 |
| Fertilizer..... | 3 | 3.51 | 3.46 | 3.49 | 3 | 3.51 | 3.49 | 3.50 |
| Alfalfa leaves. | 5 | 3.78 | 3.61 | 3.71 | 3 | 3.80 | 3.73 | 3.77 |
| Alfalfa stems . | 3 | 1.63 | 1.55 | 1.59 | 3 | 1.63 | 1.59 | 1.62 |
| Cob chop..... | 3 | 1.36 | 1.32 | 1.35 | 3 | 1.38 | 1.35 | 1.37 |
| Bone meal.... | 3 | 0.96 | 0.92 | 0.94 | 3 | 0.94 | 0.90 | 0.93 |
| Skim milk ... | 3 | 0.53 | 0.50 | 0.52 | 3 | 0.53 | 0.51 | 0.52 |
| Soil..... | 4 | 0.043 | 0.038 | 0.041 | 3 | 0.041 | 0.037 | 0.039 |

As nitrogen determinations must be made on materials differing widely in nitrogen content, it was thought well to use such a variety as one might ordinarily be called upon to analyze in everyday work. For this reason the ten different samples listed in the table were used in these determinations.

* *Jour. Ind. and Eng. Chem.*, July, 1916, 586-587.

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The figures in the table explain themselves, and as these ten samples include compounds of the highest to the lowest nitrogen content, the writer feels confident in saying that he believes sodium sulphate can be used instead of potassium sulphate when determining nitrogen in any kind of material. The analyses were carried out under exactly duplicate conditions. The period of digestion was 2 hours after the solution cleared.

Sodium sulphate, when used in the amounts mentioned, did not in any way prove objectionable in this work. It proved itself just as good an oxidizing agent as potassium sulphate and as it has a higher boiling point, it would be expected to be even better than potassium sulphate. The writer does not maintain that sodium sulphate is preferable to potassium sulphate in nitrogen determinations. There are cases where caking will take place, although this can readily be avoided by diluting as soon as cool. As far as chemical efficiency is concerned, the two chemicals compare very favorably. Where a large number of nitrogen determinations are being made and potassium sulphate is ordered in 50 and 100 pound lots, a great saving will be realized by using sodium sulphate; as much as $60 can be saved on one order of 50 pounds.

It should be mentioned here that we have found it more convenient and inexpensive to use copper wire instead of copper sulphate. As is known, the use of copper sulphate has been adopted officially for use in nitrogen determinations. Its good points have previously been discussed[1] and need no further elaboration. Pieces of copper wire approximating 0.1 gram can readily be cut with a wire cutter.

## ABSTRACTS.

**Supplies of Mangrove in Ecuador.** CONSUL GENERAL F. W. GODING. *Commerce Reports*, July 7, 1916, p. 73. In certain parts of Ecuador mangrove or red mangle logs of extreme length and diameter are plentiful. The wood has been used for years for house construction, wharves, fuel and charcoal, but no diminution of the source of supply is to be observed. The trees sometimes reach a height of 110 feet and average about 7 to 10 feet in circumference. The bark in some instances is about 1 inch in thickness and contains great quantities of tannin; it is cut in pieces and

[1] *Jour. A. O. A. C.*, I, No. 4, Part II, 18-21-23.

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exported in sacks, the present price being $0.87 to $0.96 per 100 pounds f. o. b. Guayaquil. The freight rates are approximately $35 to $37.50 per ton from Guayaquil to San Francisco and New York respectively.

**Purification of Sewage by Activated Sludge in Winter at the Sewage Testing Station, Milwaukee, Wis.** W. R. COPELAND. *Jour. Ind. and Eng. Chem.*, July, 1916, pp. 642-643. The winter temperature of Milwaukee sewage averages 51° F. with occasional drops to 40° F. or less due to melted snow. These low temperatures retard oxidation of organic matter and decrease the stability of the treated liquor. By increasing the air about 0.75 cubic foot per gallon of sewage 90 per cent. of the bacteria were removed and the suspended matter reduced to about 15 parts per 1,000,000. A table is given which shows that as the temperature of the sewage dropped the oxidation of the organic matter decreased, as indicated by the fact that nitrate in the effluent fell from 8.7 parts per 1,000,000 in October to 0.67 part per 1,000,000 in January, and the oxygen consumed increased from 19 to 31 parts per 1,000,000. The decrease in oxidation was accompanied by a decrease in stability of the effluent from 5 to 3 days. The treated liquor contained 6 parts per 1,000,000 of dissolved oxygen in winter and only a trace of nitrate, whereas in summer nitrate is high and dissolved O is low; therefore, the liquor seems to depend for its stability on nitrates in summer and dissolved oxygen in winter. The data show that good bacterial removal and clarification can be maintained at winter temperature without oxidizing the ammoniacal nitrogen into nitrates.

The activated sludge contains 98 per cent. of water and 2 per cent. of suspended solids, some of which are sticky. Centrifuges and presses used heretofore have proven unsatisfactory. A new press installed by H. R. Worthington Co. has treated the activated sludge with marked success. No lime is required, the bags do not get sticky, comparatively little power is used, and the sludge obtained can be converted into fertilizer. From the data obtained at this station it appears that 1,000,000 gallons of sewage will yield about 3,000 or 4,000 gallons of sludge containing 98 per cent. of water. When reduced to 10 per cent. of moisture this sludge will weigh about ½ ton. Assuming the nitrogen to be worth about $2 per unit the value of the sludge would range between $10 and $12 a ton. An estimate of $5 to $6 is made to convert the sludge into fertilizer and pay the freight to the consumer.

**Aeration of Sewage in the Presence of Activated Sludge.** E. J. FORT. *Jour. Ind. and Eng. Chem.*, July, 1916, pp. 634-645. The experiments of Black and Phelps at the Brooklyn Sewage Disposal Plant in 1910 were about the first to indicate a possibility of treatment with compressed air which might on further study prove to be the one sought so long. These experimenters found it possible to reduce the demand of sewage for oxygen 33 to 50 per cent. in a retention period of about 3 hours by using about 2 volumes of air per volume of sewage. A 16,000-gallon tank arranged

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for aeration experiments was put in service in the fall of 1913 as a continuously flowing sewage aerator. The first experiments were made with an air supply of 0.75 volume per volume of sewage and 2-hour retention period. It was insufficient to produce any marked results. The retention period was doubled, but with little improvement. A greater volume of air was then applied, but the results were not satisfactory, and the results secured during the winter and early spring of 1914 were not even promising. The continuous flow system was then suspended and the sewage was retained in the tank under aeration for 24-hour periods, the fill-and-draw method of operation being followed. Some phenomena of activated sludge were observed at this stage, but the principle was not then recognized as being important. This method of ripening was carried on until June, 1914, when apparently the tank had ripened and a fine clear effluent could be obtained with certainty from crude sewage or Imhoff tank effluent on the fill-and-draw plan with 24-hour aeration. During 1915 the aerator tank was rearranged for use as an activated sludge tank. A very good effluent was obtained on the fill-and-draw method of operation after 5-hour aeration with 7 volumes of air per volume of sewage. The problems met in the operation of a sewage treatment plant of this kind are very troublesome. Constant vigilance must be exercised; daily supervision by a sewage expert or scientist is required and the supplies and repairs must be provided freely. In conclusion, therefore, the engineer is not warranted in recommending for general adoption a sewage plant using this process because of its excessive cost and sensitiveness or lack of reliability.

**Activated Sludge Experiments at the Sewage Disposal Plant, Baltimore.** C. W. HENDRICK. *Jour. Ind. and Eng. Chem.*, July, 1916, pp. 645-646. Work on activated sludge experiments began during late winter. An Imhoff tank was converted so as to be suitable for use with the continuous flow activated sludge method. Carborundum, alundum, sand and cement, filtros, and unglazed tile were tested to determine the most suitable porous material through which air in small bubbles was to be admitted to the mixture of sewage and sludge. Carborundum and alundum were most acceptable because of the smallness of the bubbles and of these the carborundum was chosen because of its small cost. Tests on a small scale were carried out to determine the mixture that would produce most quickly an activated sludge, the rate at which the sewage could be purified, and the composition and other features of the sludge itself. It was proven that the absence of light had no effect on the activated sludge organisms. A sample of sludge after two months aeration had a higher nitrogen content than any determined on the ordinary sludge and more than twice as high as the average nitrogen content of ordinary digestion tank sludge.

**Composition of the Effluent Air from an Activated Sludge Tank.** F. N. CRAWFORD and EDWARD BARTOW. *Jour. Ind. and Eng. Chem.*, July,

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1916, pp. 646-647. In an effluent air an increase in the $CO_2$ and a decrease in the O is expected. $CO_2$ was determined by Hesse's method while the O was determined by absorption in alkaline pyrogallol in a Hempel double absorption pipette. Aeration was carried on for 5-hour periods and six samples were taken for each period. A decline in $CO_2$ occurs at the beginning of the aeration period and is followed by a marked increase during the remainder of the period. The rate of flow of air has little relation to the amount of $CO_2$ in the effluent air. When the content of $CO_2$ increases the amount of O is decreased by about 1 per cent., approximately 5 per cent. of the O being used up by the process. That the initial loss of $CO_2$ was due to loss of dissolved $CO_2$ was proved by aerating tap water under similar conditions. When sewage was aerated in the presence of sludge, $CO_2$ was produced by bacterial action. Fresh sewage aerated without sludge loses $CO_2$ and becomes alkaline to phenolphthalein, but on standing after the aeration period loses this alkalinity due to putrefaction and lack of air.

**Sewage Disposal Experiments at Brockton, Mass.** R. S. WESTON. *Jour. Ind. and Eng. Chem.*, July, 1916, pp. 647-648. In 1915 a small activated sludge tank was operated on the fill-and-draw plan, aeration being carried on for 4-hour periods in the presence of 25 per cent. of sludge. The effluent was then run on to sand filters and excellent results were obtained. With shorter periods of aeration the sludge becomes septic and loses its efficiency regardless of the amount of air. With greater periods not only is no nitrification produced but the accumulated suspended matter passes again into the colloidal state and the effluent from the settling tank becomes highly colored. Interesting results have been obtained through plain aeration of sewage. After two months of aeration complete nitrification had not been obtained even though 22 volumes of air per volume of sewage were used. The flow of sewage was then stopped and the aeration continued until nitrification was complete. The experiment is still in progress. Clarification was good at the beginning, but after 18 days the color of the supernatant liquor suddenly increased, the sludge began to settle imperfectly and decreased in volume. Many spent dyes from the Brockton shoe factories are present and it is believed that these are at first absorbed by the activated sludge, but prolonged aeration causes them to pass into a colloidal solution. Free ammonia is beginning to decrease and nitrites and nitrates are on the increase and it is hoped that in the end a complete nitrification and reclarification will result. The Brockton experiments have shown that the activated sludge process is the only one which offers any relief to over-worked filter beds. On the other hand they have shown that it would be impracticable to use the process alone or to produce a highly nitrified effluent thereby, though no difficulty is encountered in obtaining the latter from a bed to which the effluent from the activated sludge process is applied.

**Chemical Observations on the Activated Sludge Process as Applied to Stockyard Sewage.** ARTHUR LEDERER. *Jour. Ind. and Eng. Chem.*, July,

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1916, pp. 652-653. Experiments were conducted on the fill-and-draw plan in two 200-gallon tanks well into the cold season, being discontinued when the contents of the tanks froze. The process, being biological in nature, is greatly influenced by the temperature of the sewage. Stockyard sewage, most of which is from the packing houses, is peculiarly adapted to this process as the temperature varies between 60° and 90° F. throughout the year. The variation in discharge and composition between day and night waste is extremely marked. The free oxygen demanded is about 8 to 10 times greater than that for domestic sewage of Chicago. During the warmer seasons complete oxidation and clarification was secured with very low ammonia nitrogen and an increase of nitrite nitrogen to 5 or 10 parts per 1,000,000; in cold weather, however, absolute stabilities were only reached with ammonia nitrogen increasing several hundred per cent. and with little change in the nitrite and nitrate nitrogen. Repeated observation indicates that mere mechanical removal of the colloidal matter from sewage brings about an improvement far out of proportion to the actual percentage of substance removed. Turbidity tests in connection with the methylene-blue putrescibility test can establish a fairly definite working relation. As the turbidity increases the stability decreases, showing a deterioration of the effluent.

**Development of the Purification of Sewage by Aeration and Growths at Lawrence, Mass.** H. W. CLARK. *Jour. Ind. and Eng. Chem.*, July, 1916, pp. 653-654. In the spring of 1912, extensive experiments were begun to determine the actual purification of sewage by aeration aided by growths. For several months this work was carried on and it was found that by 24-hour aeration of sewage containing growths that a stable effluent was obtained. The sewage was emptied daily and only the growths and sewage slime left in the bottles. Later in 1912, a tank containing a number of pieces of slate separated at intervals of 1 inch or more so as to give a larger surface to which the growths might become attached was put in operation. Growths quickly collected and stable and well clarified effluents low in organic matter were obtained. The statement that the Lawrence acrating tank containing slate is a contact filter is not true, as only about 3 to 7 per cent. of the total space is filled with slate or other materials whereas in a contact filter at least 65 per cent. of the total space is filled with filtering material. A comparison of two aerated slate tanks containing sludge and growths was made with two activated sludge tanks. Both methods gave stable effluents, the slate tank method requiring generally more time to accomplish this result but less air and the effluent of the activated sludge tank being the clearer in appearance. During the winter, the work was carried on at lower temperatures, the slate tanks producing a slightly more stable effluent than that produced by the activated sludge tanks. The governing factors for success in this process are the cost of power for supplying the large volume of air necessary and a sewage that readily yields itself to this method of treatment.

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## PATENTS.

**Leather Working Machine. U. S. Patent 1,187,694.** W. C. WRIGHT, Lynn, Mass., assignor to Bosler Machinery Co., Lynn, Mass.

**Machine for Brushing Leather. U. S. Patent 1,188,561.** CARLETON RUHE, Olean, N. Y.

**Leather Staking Machine. U. S. Patent 1,189,975.** ALFRED C. LAYMAN, Wilmington, Del.

**Flexible Leather Board Composition. U. S. Patent 1,188,600.** ALFRED ADAMS, JR., Philadelphia, Pa. A mixture of hide and leather clippings, 90 pounds, cotton 10 pounds, and a liquid binder, the entire mixture being shredded, beaten and stirred to produce a homogeneous mass which is molded into shape, subjected to high pressure and slowly dried.

**Material Adapted for Use in the Manufacture of an Imitation Leather. U. S. Patent 1,190,806.** W. O. STODDARD, JR., Madison, N. J., assignor to The Duratex Co., Newark, N. J.

**Material Adapted for Use in the Manufacture of an Imitation Leather and Method of Making the Same. U. S. Patent 1,190,807.** W. O. STODDARD, JR., Madison, N. J., assignor to The Duratex Co., Newark, N. J.

**Tanning Vats. British Patent 3,484.** E. WILSON, Lancashire, England. Machine for tanning butts or hides in which the latter are fastened to slats constituting the periphery of a drum which rotates in a vat with a semi-cylindrical bottom, in which the tanning liquor is automatically maintained at the required strength, the hides being conveyed through the liquor practically edgeways.

**Tanning. British Patent 100,163.** H. MORIN, St. Denis, France. A white leather is obtained by immersing the skins in a solution of silica and subsequently precipitating the silica. Any silicate may be used, but preferably the silicate of soda or potash, and a suitable precipitant is acetic acid. This process may be used with other processes, and the leather obtained dyed or otherwise treated or kept for treatment by soaking in brine, glycerine, or other suitable material.

**Treating Glove Leather. British Patent 100,311.** SOC. ANON. DES GANTS ALEXANDRE, 15, Rue Rochechouart, Paris. Leather used in glove manufacture is treated to render it immune from attack by bacteria in cutaneous exudations, with organic derivatives of salicylic and benzoic acids. The leather is placed in a bath containing methylic or ethylic ethers of benzoic acid or methylic, ethylic, amylic, or phenylic ethers of salicylic acid, mixed with odor-masking substances and salted eggs. Before dipping into the bath, the leather is purged, after tawing and before dyeing, in an acid bath to eliminate alkalies and salts, formic and lactic acids being preferably used, and then passed through an alum bath and washed.

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## RESEARCH LABORATORY.

The following form for subscriptions to the fund for the establishment of the Research Laboratory in connection with the Tanners' Institute is being sent out to tanners generally. The

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plan seems to be a very fair one, and it is to be hoped that the responses will be prompt and numerous.

TANNERS' INSTITUTE FUND.

I—We .....

of the City of.....State of.....
do hereby agree to pay to Tanners' Institute Fund, The National Association of Tanners, Custodians, on or before September 1 of the years 1916 to 1920 inclusive, my—our pro-rated share of $15,000 per annum, provided that not less than seventy-five other members of the Leather Industry similarly subscribe to this fund, and provided that my—our share per annum shall not exceed ($ *)..... Dollars.

Signed this .....day of.....1916, in the City of.....State of.....

.....

.....

.....

* See over. Our Class is.....

(*Reverse*)

The share of each subscriber will be determined on the basis of the following table:

| Value of sales or production | Class | Number of shares |
|---|---|---|
| 0– 200,000 | A | 1 |
| 200,000– 500,000 | B | 2 |
| 500,000– 1,000,000 | C | 3 |
| 1,000,000– 5,000,000 | D | 5 |
| 5,000,000–10,000,000 | E | 8 |
| 10,000,000–15,000,000 | F | 12 |
| 15,000,000–25,000,000 | G | 18 |
| 25,000,000 and over | H | 30 |

The size of the share will vary with the number of subscribers and the total size of their business. With seventy-five subscribers and the census of 1909 showing 48.2 per cent. of the total value of the leather produced in the industry by establishments in Class D or greater, the shares will be about $50 each.

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# BIOCHEMICAL STUDIES OF SKIN.

*By George J. Rosenthal,*

Dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

Since skin is of a biological nature, the study of the changes it undergoes—due to the several processes in use in the tannery—naturally falls to the lot of the bio-chemist. In fact, it would appear that the best solutions of many of the problems connected with tanning could be affected only by a comparative bio-chemical and historical study.

Little work has been done on the chemistry of skin. Almost nothing is known regarding the changes produced in skin either in tanning or in the processes preparatory to tanning—in soaking, in liming and in bating. We have undertaken this work in the hope of obtaining information that would give us a deeper insight into the various factors involved in the preparation of leather.

In the structure of the skin of vertebrates, many different substances occur, such as the constituents of the epidermis, the connective and fatty tissues, muscles and nerves.

The cells of the corneous layer show, according to their age, different resistance to reagents, especially alkalies. The younger the cell the less resistant it is to the action of alkali. The resistance increases with age and the cell membranes of many corneous formations are almost insoluble in caustic alkalies. According to Unna,[1] three different substances are found in horny material, A-, B- and C-keratin. A-keratin, which forms the envelope of the horn and hair cells and the outer layer of the hair, is not dissolved by fuming nitric acid and does not give the xanthoproteic test. The B-keratin, occurring in the nail cells and the C-keratin give the xanthoproteic test, but the former, unlike the latter is soluble in fuming nitric acid.

It is difficult to isolate keratin from tissues in a pure condition without some decomposition. This, together with the fact that there are probably a number of different keratins, would help to explain the wide variations in the recorded data for the elemen-

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tary composition of keratin. The analyses of a few keratins and of tissues rich in keratin are given:

| | C | H | N | S | O | |
|---|---|---|---|---|---|---|
| Human hair ... | 43.72 | 6.34 | 15.06 | 4.95 | 29.93 | Rutherford and Hawk[2] |
| Nail..... | 51.00 | 6.94 | 17.51 | 2.80 | 21.75 | Mulder[3] |
| Neurokeratin ... | 56.11–58.45 | 7.26-8.02 | 11.46–14.32 | 1.63-2.24 | — | Kühne[4] |
| Neurokeratin ... | 56.61 | 7.45 | 14.17 | 2.27 | — | Argiris[5] |
| Horn..... | 50.86 | 6.94 | — | 3.20 | — | Horbaczewski[6] |
| Tortoise shell... | 54.89 | 6.56 | 16.77 | 2.22 | 19.56 | Mulder[3] |
| Shell membrane | 49.78 | 6.64 | 16.43 | 4.25 | 22.50 | Lindwall[7] |

Mohr[10] has determined the quantity of sulphur in various keratin substances. Sulphur is found in loose chemical combination and is removed chiefly by the action of alkalies as sulphides or in part by boiling water. On heating keratin with water in sealed tubes to a temperature of 150° C. or higher, keratin dissolves with the elimination of sulphureted hydrogen or of mercaptan and the solution contains proteose-like substances called atmidkeratin and atmidkeratose (Bauer[8]).

Fischer and Dorpinghaus[9] have found glycocoll, alanine, valine, proline, serine, phenylalanine, and pyrrolidone-carboxylic acid among the decomposition products of horn substances in addition to leucine, lysine, tyrosine, arginine, glutamic acid and aspartic acid. K. Morner[10] showed that cystine was present in the cleavage products. He obtained from ox-horn, human hair, and the shell membrane of hen's egg 6.8, 13.92, and 7.62 per cent. of cystine calculated on the dry basis. Buchtala[11] obtained the following amounts of cystine from various keratins: Human hair, 12.98-14.53 per cent.; nails, 5.15; horse hair, 7.98; horse hoofs, 3.20; ox hair, 7.27; ox hoofs, 5.37; pig bristles, 7.22; pig hoofs, 2.17; elephant epidermis, 4.7. Morner concludes that at least in ox horn and in human hair all the sulphur exists as cystine. The large quantity of cystine in the keratins is considered especially characteristic and they differ in this regard from other proteins.

The keratins differ among themselves in composition and do not apparently form a characteristic group. It is possible that the differences in composition of the several keratins may be due to differences in the purity of the substances examined.

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| | Keratin from horse hair | Keratin from sheep wool | Keratin from sheep horn | Shell membrane of hen's egg |
|---|---|---|---|---|
| Glycocoll | 4.7 | 0.58 | 0.45 | 3.9 |
| Alanine | 1.5 | 4.40 | 1.60 | 3.5 |
| Valine | 0.9 | 2.80 | 4.50 | 1.1 |
| Leucine | 7.1 | 11.50 | 15.30 | 7.4 |
| Serine | 0.6 | 0.10 | 1.10 | — |
| Aspartic acid | 0.3 | 2.30 | 2.50 | 1.1 |
| Glutamic acid | 3.7 | 12.90 | 17.20 | 8.1 |
| Cystine | 7.98 | 7.30 | 7.50 | 7.62 |
| Phenylalanine | 0.0 | — | 1.90 | — |
| Tyrosine | 3.2 | 2.90 | 3.60 | 0.0 |
| Proline | 3.4 | 4.40 | 3.70 | 4.0 |
| Histidine | 0.61 | — | — | — |
| Arginine | 4.45 | — | 2.70 | — |
| Lysine | 1.12 | — | 0.20 | — |

Keratin is insoluble in water, alcohol or ether. It dissolves when heated with water to 150°-200° C. It also dissolves in caustic alkalies, especially on heating. It is not dissolved by artificial gastric or pancreatic solutions. In the preparation of keratin, the finally divided substance is first treated with boiling water, then with dilute acid, pepsin-hydrochloric acid, alkaline pancreatic juice, water, alcohol and ether.

The connective tissues consist of both living and lifeless matter. These tissues consist of cells, but they also contain a large amount of protein matter in a fibrous condition and resistant to most reagents. There are several kinds of connective tissue fibers. We may readily distinguish the yellow and white forms. The yellow fibers are tough and elastic, consisting largely of a protein called elastin. The white fibers are tough but non-elastic, consisting largely of collagen. The characters of the cells and of the surrounding groundwork differ in the several connective tissues.

Elastin may be prepared from the *ligamentum nuchae*. The tissue is extracted under thymol for 3-4 days with 5 per cent. NaCl to remove albumins and globulins, and then repeatedly treated with boiling water to gelatinize and remove the collagen. The residue is thoroughly washed with water, extracted with alcohol and ether, and dried.

Elastin was at one time considered to be free from sulphur, but it has been shown by Richards and Gies[12] that elastin con-

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tains 0.14 per cent. sulphur with a nitrogen content of 16.87 per cent. Hammarsten questions whether elastin is a unit substance.

The hexone bases have been found among the hydrolytic products of elastin, but only in small quantities. Richards and Gies found that the basic nitrogen represented only 3.34 per cent. of the total nitrogen. On heating with water in sealed tubes, or boiling with dilute acids, or by the action of proteolytic enzymes, elastin is decomposed into two products called hemielastin and elastinpeptone by Horbaczewski, and protoelastose and deuteroelastose by Chittenden and Hart. Protoelastose is soluble in cold water and separates out on heating; it is precipitated by mineral acids, as well as by acetic acid and potassium ferrocyanide. A solution of deuteroelastose does not become cloudy on heating, and is not precipitated by the above reagents.

Pure elastin is resistent towards the action of chemical reagents and is insoluble in water, alcohol and ether. It is slowly dissolved by boiling alkali, by cold concentrated sulphuric acid, and easily dissolved in strong, warm, nitric acid. The behavior of elastin towards cold concentrated hydrochloric acid depends upon its source. Elastin from the aorta dissolves readily in the reagent while that from the *ligamentum nuchae,* at least from old animals, dissolves with difficulty. Elastin is more easily attacked by warm concentrated hydrochloric acid. It responds to the xanthoproteic and Millon reactions but not to the Hopkins-Cole test.

Collagen is the chief constituent of the fibrils of white connective tissue. Collagens from different tissues vary in composition and there are probably several varieties.

| | C | H | N | S | O | |
|---|---|---|---|---|---|---|
| Collagen..... | 50.75 | 6.47 | 17.86 | — | 24.92 | Hofmeister[13] |
| Gelatin (com.).... | 49.88 | 6.80 | 17.97 | 0.70 | 25.13 | Chittenden[14] |
| Gelatin from tendons..... | 50.11 | 6.56 | 17.81 | 0.26 | 25.26 | Van Name[15] |
| Gelatine from ligaments .... ..... | 50.49 | 6.71 | 17.90 | 0.57 | 24.33 | Richards and Gies[12] |
| Fish glue..... | 48.69 | 6.76 | 17.69 | — | -- | Faust[16] |

By prolonged treatment with boiling water, especially in the presence of a little acid, collagen is converted into gelatin. However, on heating gelatin to 130° C., Hofmeister found that he

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could transform it to collagen and considers the latter as the anhydride of gelatin. On decomposition, gelatin yields neither tyrosine nor tryptophane but does yield considerable glycocoll. Hausmann[17] found that the yield of basic nitrogen was 35.83 per cent. of the total nitrogen.

Collagen is insoluble in water, salt solutions, dilute acids, and alkailes, but swells up in dilute acids. Collagen is dissolved by gastric juice and also by pancreatic juice if it has been previously heated with water above 70° C. or treated with acid. (Kühne and Ewald.[18])

Gelatin is colorless and transparent in thin layers. It dissolves in warm water with the formation of a sticky liquid, which solidifies on cooling, if sufficiently concentrated. It swells in cold water but does not dissolve. It was shown by Pauli and Rona[19] that sulphates, citrates, acetates and glycerin accelerate the gelatinization of gelatin, while chlorides, chlorates, bromides, alcohol, and urea retard this action.

Solutions of gelatin are not precipitated on boiling, by mineral or acetic acids, alum, basic lead acetate, or by metallic salts in general. A solution of gelatin, acidified with acetic acid, may be precipitated by potassium ferrocyanide if the reagent is added with care. Tannic acid, in the presence of salt, will precipitate gelatin from a solution, and according to Trunkel,[20] this reaction is quantitative if the proportions of gelatin and tannic acid are 10-7. Trunkel claims that this reaction is an adsorption phenomenon and is not due to a true chemical combination.

Aqueous solutions of gelatin are precipitated by acetic acid and NaCl; mercuric chloride in the presence of HCl and NaCl; metaphosphoric acid and phosphomolybdic acid in the presence of acid; and especially alcohol in the presence of neutral salts. Gelatin solutions do not diffuse. Gelatin gives the biuret but not the Hopkins-Cole reaction. It gives faint Millon and xanthoproteic tests. These may be due to protein impurities, although Morner claims that he obtained a good Millon reaction if the reagent is not added in excess.

On prolonged treatment with boiling water, especially in the presence of dilute acid, also in gastric and peptic digestion, gelatin is transformed into gelatoses and gelatin peptones, which diffuse more or less readily.

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Tables of the hydrolytic products of elastin and collagen are given below. The former is cited from Abderhalden and Rona,[21] and the latter from Fisher, Levene and Aders,[22] and Levene and Beatty.[23]

| | Elastin | Gelatin |
|---|---|---|
| Glycocoll | 25.75 | 16.5 |
| Alanine | 6.58 | 0.8 |
| Valine | 1.4 | 1.0 |
| Leucine | 21.38 | 2.1 |
| Proline | 1.74 | 5.2 |
| Phenylalanine | 3.89 | 0.4 |
| Aspartic acid | — | 0.56 |
| Glutamic acid | 0.76 | 1.88 |
| Serine | — | 0.4 |
| Cystine | — | — |
| Tyrosine | — | — |
| Arginine | 0.3 | 7.62 |
| Histidine | — | 0.4 |
| Lysine | — | 2.75 |

Mucin, or mucoid substances occur not only in the salivary glands and skin, but also in the various connective tissues. Mucoid is a constant constituent of the skins of the amphibia and fishes and occurs subcutaneously in man in a disease of the thyroid gland, myxoedema.

| | C | H | N | S | O | |
|---|---|---|---|---|---|---|
| Tendon mucoid.. | 48.76 | 6.53 | 11.75 | 2.33 | 30.63 | Chittenden and Gies |
| Tendon mucoid.. | 47.47 | 6.68 | 12.58 | 2.20 | 31.07 | Cutter and Gies[24] |
| Osseomucoid .... | 47.07 | 6.69 | 11.98 | 2.41 | 31.85 | Hawk and Gies[25] |

The relation between mucin and mucoid is still uncertain but the latter contains more sulphur than the former. The chemistry of mucin is not well understood, but extensive studies have been made by Gies and his collaborators, and by Levene[26] on tendomucoid. Mucoids are glycoproteins and yield carbohydrate on hydrolysis. Levene decomposed tendomucoid by acid hydrolysis and obtained sulphuric acid, galactose and galactosamine. On decomposition by stronger acid he obtained leucine, tyrosine, acetic and levulinic acids. On peptic digestion, proteoses and peptone-like substances, still containing the carbohydrate group, are obtained. On tryptic digestion, leucine, tyrosine and tryptophane are found (Posner and Gies[27]). The glucosamine is only split off after strong hydrolysis with acid. Müller[28] obtained 35

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per cent. glucosamine from mucous membrane mucin and 23.5 per cent. from submaxillary mucin. Certain mucins, such as the submaxillary mucin, are easily changed by dilute alkali (*e. g.*, lime water), while others, such as tendomucoid, are not affected. If submaxillary mucin is treated with 5 per cent. KOH, alkali albuminate is obtained in addition to proteoses, peptones and substances of an acid nature, which have reducing powers.

The mucins, like the nucleins, are acid substances. They are soluble in dilute alkali and are precipitated by dilute acid. They are soluble in stronger acids. They are prepared by extraction of tissues with dilute alkali, followed by acidification of the extract with acetic acid. Such preparations generally contain nucleoprotein. Salivary mucins exist in the submaxillary gland as the potassium salt. Cartilage mucoid probably occurs as the calcium salt.

## Studies of Dogskin.

In order to learn whether there are any material differences in the composition of skin taken from several parts of the animal, the skin of a healthy young dog was removed one hour after death and was cut into "butt," "shoulder," and "bellies." The pieces were immediately placed in a vacuum oven and dried at 55°-60° C. under a vacuum of 29 inches. After 8 hours, the skin was sufficiently dry to be easily cut into small pieces and ground to a powder in a hashing machine. Samples of the ground material (3.5-4.0 grams each) were placed in stoppered bottles with 150 cc. of a 10 per cent. solution of sodium chloride under toluol and incubated at 37° C. The solutions were renewed daily until no coagulable protein could be obtained. Two changes, or a total of 450 cc. of solvent were usually found to be sufficient. The combined solvents were heated with the addition of a few drops of acetic acid. The coagulum of albumin and globulin was washed with warm water, alcohol and ether and weighed.

The residual skin was washed with water and extracted under toluol with 150 cc. of half saturated lime water. Three changes of solvent were made, using a total volume of 600 cc. The combined solvents were neutralized to phenolphthalein with 10 per

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cent. hydrochloric acid and acidified with 0.2 per cent. hydrochloric acid. The precipitated mucoid was washed with 0.2 per cent. hydrochloric acid, water, alcohol and ether, dried and weighed. The filtrates were in all cases tested with additional acid for unprecipitated mucoid. (In our subsequent work this technic was changed in so far as the wash water was made of the same degree of acidity as the original solution from which the mucoid was precipitated.)

The washed skin residue was subjected to an alkaline tryptic digestion under toluol at 37° C. After 24 hours, the solution was decanted and the digestion was continued for 96 hours with fresh pancreatin. Nitrogen in the combined filtrates was determined by the Kjeldahl method and was multiplied by the factor 6 for elastin. A correction was made for the nitrogen of the enzyme.

The washed skin residue was then digested in a pepsin –0.2 per cent. hydrochloric acid solution, following the methods as given above for the determination of elastin. The factor used was 5.58, since collagen contains 17.90 per cent. of nitrogen (Richards and Gies). Keratin and residue were subtracted from 100.

In selecting these methods, no claim is made that they are entirely satisfactory; for example, it has been shown by Posner and Gies that in extracting globulin by the use of a solution of sodium chloride, small amounts of mucoid may be extracted at the same time. In fact, it was noticed that sometimes the filtrates, after the removal of the coagulated protein, had an opalescent appearance. Studies of these filtrates are indicated and may prove instructive. Since we do not know whether skin collagen and skin elastin are identical with similar tissues obtained elsewhere, it is possible that there is a slight error in calculating the amounts of these substances. These errors are constant throughout the experiments and do not affect them in the ultimate analysis. We feel that the methods employed are the best available in the light of our present knowledge.

The composition of the skin taken from three different parts of the dog varied extensively, as can be readily noticed from an examination of the following table:

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ANALYSIS OF DOGSKIN.

| | Shoulder Per cent. | Belly Per cent. | Butt Per cent. |
|---|---|---|---|
| Water | 37.32 | 35.67 | 37.25 |
| Solids | 62.68 | 64.33 | 62.75 |
| Fat | 29.67 | 34.82 | 37.84 |
| Protein | 33.02 | 29.27 | 24.90 |
| Ash | 0.62 | 0.48 | 0.38 |
| PROTEINS. | | | |
| Coagulable protein | 6.88 | 7.74 | 6.04 |
| Mucoid | 0.80 | 0.85 | 1.26 |
| Elastin | 1.51 | 3.53 | 1.29 |
| Collagen | 20.52 | 13.59 | 12.29 |
| Keratin | 3.31 | 3.56 | 4.02 |

## STUDIES OF CALFSKIN.

Our object in these experiments was to study not only the composition of calfskin taken from different parts of the body but also to ascertain the changes that were effected in these parts in the processes preliminary to tanning.

For this series of experiments, the skin of a 5-weeks old, milk-fed calf was removed in the slaughter house 1 hour after the death of the animal. The skin, weighing 8 pounds, was divided into shoulder, bellies and butt as in the case of the dog skin. The pieces were soaked in water for 42 hours, and then placed in lime water, using 5 per cent. slaked lime calculated on the basis of the weight of the skins and adding 2½ per cent. more lime after 24 hours. The pieces of skin were unhaired on the fifth day, washed and bated with oropon. Samples were cut in duplicate from opposite corners of the pieces. The samples were taken from

1. Fresh skin.
2. Skin after 42 hours' soaking.
3. Skin after 24 hours' liming.
4. Skin after 66 hours' liming.
5. Skin after 120 hours' liming and unhairing and washing.
6. Skin after bating.

The samples were dried, cut, ground and extracted, following the methods used in the analysis of dogskin. The percentages of coagulated protein, elastin, mucoid, collagen and keratin are reported on the dry basis.

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FIG. 1.
Normal calfskin × 150.

A—Corneous layer. B—Malpighian layer. C—Papillary layer. D—Reticular layer.
E—Hair shaft. F—Hair follicle. G—Sebaceous. H—Hair.
I—Inner root sheath. O—Outer root sheath.

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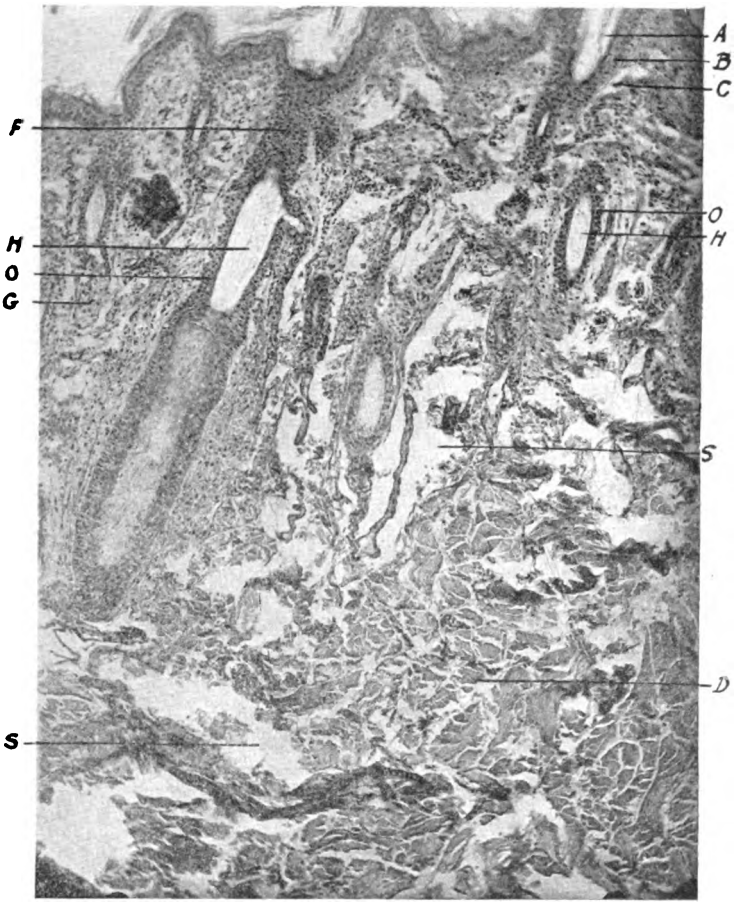


FIG. 2.
Calfskin after soaking 42 hours in water × 150.

A—Corneous layer. B—Malpighian layer. C—Papillary layer. D—Reticular layer.
F—Hair follicle. G—Sebaceous gland. H—Hair. O—Outer root sheeth.
S—Shrinkage space.

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**FIG. 3.**
**Calfskin after 24 hours in lime water × 150**

**B—Malpighian layer. C - Papillary layer. D—Reticular. $F^1$—Degenerating hair follicle.**

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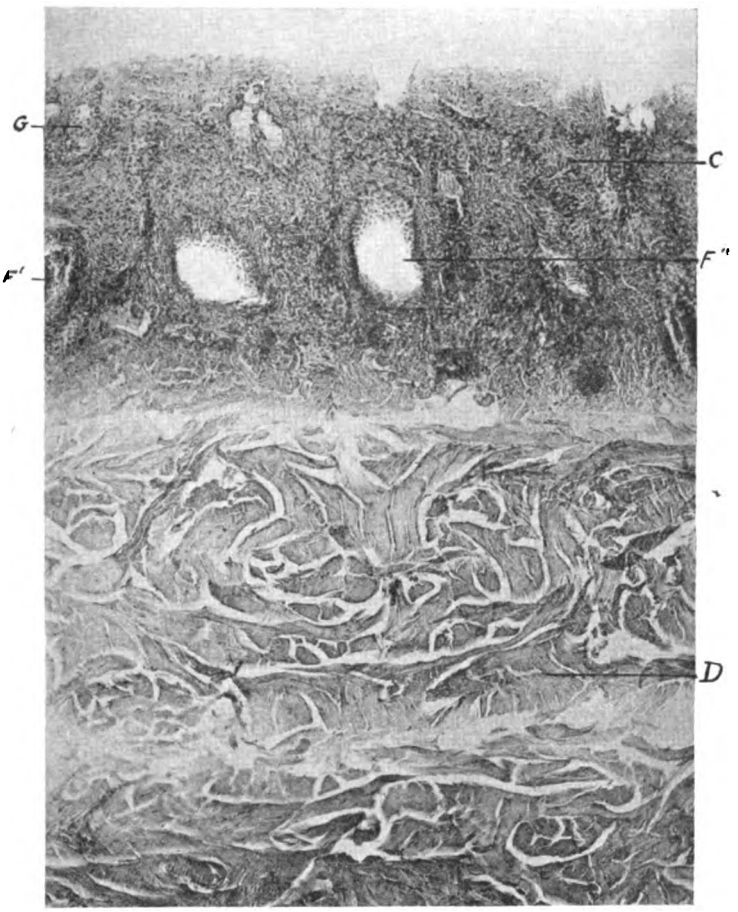


FIG. 4.
Calfskin after 66 hours in lime water × 150.

C—Papillary layer. D—Reticular layer. $F^{I}$—Degenerating follicle $F^{II}$—Empty follicle.
G—Gland.

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FIG. 5.
Calfskin unhaired after 120 hours in lime water × 150.

C—Papillary layer. D—Reticular layer. F¹—Degenerating hair follicles.
F¹¹—Empty hair follicles.

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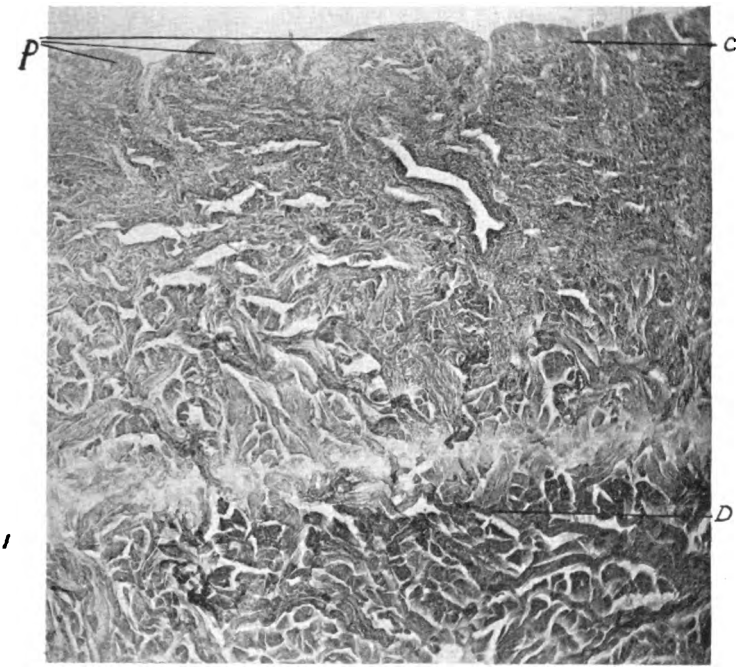


FIG. 6.
Calfskin after bateing × 150.

C—Papillary layer. D—Reticular. P—Papillae.

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No. 1.—Analysis of Calfskin.

| | Belly Per cent. | Butt Per cent. | Shoulder Per cent. |
|---|---|---|---|
| Coagulable protein | 4.30 | 4.14 | 5.16 |
| Elastin | 19.43 | 12.31 | 16.74 |
| Mucoid | 1.24 | 4.81 | 2.29 |
| Collagen | 51.46 | 58.83 | 39.66 |
| Keratin | 25.73 | 19.91 | 36.15 |

No. 2.—Calfskin After Soaking 42 Hours in Water.

| | | | |
|---|---|---|---|
| Coagulable protein | 4.67 | 7.18 | 5.37 |
| Elastin | 19.72 | 11.75 | 15.04 |
| Mucoid | 1.07 | 4.56 | 2.11 |
| Collagen | 50.75 | 53.00 | 46.88 |
| Keratin | 23.79 | 17.31 | 30.60 |

No. 3.—Calfskin After 24 Hours in Lime Water.

| | | | |
|---|---|---|---|
| Coagulable protein | 3.81 | 4.64 | 11.87 |
| Elastin | 19.08 | 13.06 | 14.65 |
| Mucoid | 1.07 | 3.65 | 1.76 |
| Collagen | 56.47 | 62.88 | 43.61 |
| Keratin | 19.57 | 15.77 | 28.11 |

No. 4.—Calfskin After 66 Hours in Lime Water.

| | | | |
|---|---|---|---|
| Coagulable protein | 7.45 | 5.96 | 9.25 |
| Elastin | 10.34 | 9.15 | 14.60 |
| Mucoid | 1.10 | 2.29 | 1.58 |
| Collagen | 63.01 | 66.78 | 54.43 |
| Keratin | 18.10 | 15.82 | 20.14 |

No. 5.—Calfskin Unhaired After 120 Hours in Lime Water.

| | | | |
|---|---|---|---|
| Coagulable protein | 9.88 | 8.55 | 10.00 |
| Elastin | 8.92 | 10.36 | 5.55 |
| Mucoid | 0.93 | 2.42 | 0.85 |
| Collagen | 78.90 | 76.93 | 82.08 |
| Keratin | 1.37 | 1.74 | 1.52 |

No. 6.—Calfskin After Bating.

| | | | |
|---|---|---|---|
| Coagulable protein | 14.81 | 10.02 | 5.66 |
| Elastin | 0.85 | 0.31 | 0.00 |
| Mucoid | 0.94 | 0.82 | 0.34 |
| Collagen | 82.85 | 87.71 | 93.81 |
| Keratin | 0.75 | 1.14 | 0.19 |

The question of the changes of the ash content was undertaken at the same time. Studies were made of the changes of the total ash and of the ash found in the coagulable protein, mucoid and keratin.

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STUDIES OF THE TOTAL ASH CONTENT.

| Experiment | Belly Per cent. | Butt Per cent. |
|---|---|---|
| 1. | 1.88 | 1.53 |
| 2. | 0.98 | 0.98 |
| 3. | 4.39 | 5.30 |
| 4. | 6.80 | 6.76 |
| 5. | 3.18 | 3.68 |
| 6. | 2.02 | 1.23 |

It will be noticed that the ash content is lowered in soaking and rises during liming. The drop seen in experiment No. 5 may be explained chiefly by the fact that the analysis was made after the skin was unhaired. A noticeable loss is observed after bating.

ASH IN COAGULABLE PROTEIN, CALCULATED ON THE DRY WEIGHT OF THE COAGULUM.

| | Belly Per cent. | Butt Per cent. |
|---|---|---|
| 1. | 35.28 | 25.60 |
| 2. | 17.34 | 10.59 |
| 3. | 25.72 | 34.70 |
| 4. | 49.66 | 57.72 |
| 5. | 19.64 | 26.43 |
| 6. | 11.69 | 8.78 |

ASH IN MUCOID, CALCULATED ON THE DRY WEIGHT OF THE MUCOID.

| | | |
|---|---|---|
| 1. | 1.61 | 1.66 |
| 2. | 1.86 | 0.66 |
| 3. | 11.20 | 10.41 |
| 4. | 17.27 | 26.20 |
| 5. | 6.45 | 2.89 |
| 6. | 3.19 | 2.44 |

ASH IN KERATIN, CALCULATED ON THE DRY WEIGHT OF THE KERATIN.

| | | |
|---|---|---|
| 1. | 1.36 | 1.96 |
| 2. | 0.63 | 1.10 |
| 3. | 16.81 | 22.26 |
| 4. | 16.08 | 21.22 |
| 5. | 86.13 | 77.58 |
| 6. | 34.67 | 28.95 |

ASH IN COAGULABLE PROTEIN, CALCULATED ON THE DRY WEIGHT OF THE SKIN.

| | | |
|---|---|---|
| 1. | 1.51 | 1.06 |
| 2. | 0.81 | 0.76 |
| 3. | 0.98 | 1.61 |
| 4. | 3.70 | 3.44 |
| 5. | 1.94 | 2.26 |
| 6. | 1.73 | 0.88 |

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ASH IN MUCOID, CALCULATED ON THE DRY WEIGHT OF THE SKIN.

| | | |
|---|---|---|
| 1. | 0.02 | 0.08 |
| 2. | 0.02 | 0.03 |
| 3. | 0.12 | 0.38 |
| 4. | 0.19 | 0.60 |
| 5. | 0.06 | 0.07 |
| 6. | 0.03 | 0.02 |

ASH IN KERATIN, CALCULATED ON THE DRY WEIGHT OF THE SKIN.

| | | |
|---|---|---|
| 1. | 0.35 | 0.39 |
| 2. | 0.15 | 0.19 |
| 3. | 3.29 | 3.51 |
| 4. | 2.91 | 2.72 |
| 5. | 1.18 | 1.35 |
| 6. | 0.26 | 0.33 |

Upon inspection of these tables the following items may be noticed: 1. The steady rise in the amounts of coagulable protein, due perhaps to the breakdown of cellular material and to the formation of metaprotein. 2. Skin from the butt contains more mucoid than skin taken from other parts. This fact may also be noticed in the case of dogskin. 3. There appears to be a loss of mucoid in liming. This fact can be more easily noticed in the shoulder series where there is a decline from experiment No. 2 to experiment No. 6, *viz:* 2.11 per cent., 1.76 per cent., 1.58 per cent., 0.85 per cent. 4. In bating, the elastin is digested.

Studies were made at the same time on the water content of calfskin in the several processes mentioned above.

PERCENTAGE OF WATER IN CALFSKIN.

| Experiment | Belly Per cent. | Butt Per cent. | Shoulder. Per cent. |
|---|---|---|---|
| 1. | 66.29 | 61.26 | 64.42 |
| 2. | 73.73 | 73.16 | 75.59 |
| 3. | 84.77 | 77.45 | 82.14 |
| 4. | 80.07 | 82.81 | 80.92 |
| 5. | 81.24 | 78.65 | 77.42 |
| 6. | 78.65 | 76.95 | 73.39 |

It will be noticed that water is absorbed in soaking and during the early periods of liming. This period of maximum swelling is followed by a gradual loss of water; the bated skin containing more water than the soaked skin.

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## Studies of Kid and Cabretta Skins.

These skins were obtained in the open market in a dried condition. The butts only were used in these experiments and samples were analyzed after the following treatment:

1. Dry skin.
2. After 4 days soaking in water.
3. After immersion of 2 days in lime water and $Na_2S$.
4. After immersion of 7 days in lime water and $Na_2S$.
5. After immersion of 15 days in lime water and $Na_2S$.
6. After bating with Oropon.

The technic followed was the same as used in our previous experiments on dog and calf skins, and the results are reported on the dry basis.

No. 1.—Analysis of Dry Skins.

| | Kid Per cent. | Cabretta Per cent. |
|---|---|---|
| Coagulable protein | 2.20 | 2.49 |
| Mucoid | 5.97 | 11.97 |
| Elastin | 4.78 | 4.49 |
| Collagen | 43.71 | 50.34 |
| Keratin | 43.34 | 30.71 |

No. 2.—Skins After Soaking 4 Days in Water.

| | | |
|---|---|---|
| Coagulable protein | 4.29 | 5.28 |
| Mucoid | 4.87 | 12.87 |
| Elastin | 4.71 | 6.50 |
| Collagen | 45.62 | 48.41 |
| Keratin | 40.51 | 26.94 |

No. 3.—Skins After 2 Days in Lime Water and $Na_2S$.

| | | |
|---|---|---|
| Coagulable protein | 2.75 | 3.19 |
| Mucoid | 4.73 | 10.40 |
| Elastin | 4.42 | 4.20 |
| Collagen | 54.16 | 57.05 |
| Keratin | 33.94 | 25.16 |

No. 4.—Skins After 7 Days in Lime Water and $Na_2S$.

| | | |
|---|---|---|
| Coagulable protein | 3.70 | 2.41 |
| Mucoid | 4.47 | 7.34 |
| Elastin | 3.96 | 4.19 |
| Collagen | 74.10 | 66.66 |
| Keratin | 13.77 | 19.40 |

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No. 5.—Skins Unhaired After 15 Days in Lime Water and $Na_2S$.

| | | |
|---|---|---|
| Coagulable protein | 4.53 | 6.30 |
| Mucoid | 2.78 | 3.61 |
| Elastin | 4.54 | 3.27 |
| Collagen | 87.13 | 86.00 |
| Keratin | 1.02 | 0.82 |

No. 6.—Skins After Bating.

| | | |
|---|---|---|
| Coagulable protein | 6.97 | 10.88 |
| Mucoid | 0.00 | 0.95 |
| Elastin | 0.00 | 0.00 |
| Collagen | 92.38 | 87.57 |
| Keratin | 0.65 | 0.60 |

These studies of kid and cabretta skins bear out our conclusions based on the study of calfskin. The rise in coagulable protein, the loss of mucoid and the digestion of elastin may again be noted.

The question of the changes of the water content was next undertaken with the following results:

Studies of the Water Content of Skins.

| Experiment | Kid Per cent. | Cabretta Per cent. |
|---|---|---|
| 1. | 11.62 | 11.58 |
| 2. | 67.49 | 73.00 |
| 3. | 73.58 | 74.00 |
| 4. | 81.25 | 81.00 |
| 5. | 80.78 | 80.35 |
| 6. | 65.76 | 73.60 |

Here, as in the case of calfskin, the curve rises to a maximum in the earlier periods of liming and then drops. In these experiments the water content of the bated skins was approximately that of the soaked skins.

## Summary.

1. Studies were made of the composition of dog, calf, kid and cabretta skins.

2. Studies were made of the changes of composition of calf, kid, and cabretta skins that were affected in soaking, in liming and in bating.

Due to imperfect technic, perhaps, the histological side of the question has been almost entirely neglected. The structure of

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skin has been fairly well established. What happens to the various layers, is a question that has not yet been answered.

The integument, the term including the skin and all the structures derived from it, is a resisting, protective coat closely investing the entire body. The integument consists of two layers, the outer, epidermis and the inner, corium (*derma*). The epidermis is derived from the ectoderm and the corium from mesenchyme.[29]

The epidermis[30] is a thin pellicle covering the superficial surface of the corium. The under surface of the epidermis is alternately raised and lowered into a system of furrows and depressions, moulding on to the upper surface of the corium, filling up the spaces between the papillae, and dipping into the follicles and excretory ducts of the glands. The external face of the epidermis is covered with hair.

Two layers of cells are present in the epidermis. At the base, next to the corium is the Malpighian layer (*stratum germinativum* or *mucosum*) above which is found the outer horny layer, the *stratum corneum*. In the horse, the two layers are not very distinct from each other. (Chauveau[31]).

The Malpighian[32] layer may be subdivided into three parts according to the characteristics of its cells. First, the basal layer consisting of columnar cells resting on the corium; second, the middle layer, consisting of polygonal cells arranged in several strata, the number varying according to the region of the body; and third the upper layer or *stratum granulosum* which is composed of two or three layers of gradually flattening cells characterized by peculiar granules. These granules, called Keratohyalin[34], occur in the form of irregular bodies imbedded in the protoplasm. The cell nuclei show degenerative processes and it is possible that the keratohyalin is derived from the fragments of the dying nucleus (Böhm and Davidoff).

The cells of the Malpighian layer are attached to other cells, more or less distant, by fine, thread-like processes. It has been shown that these processes meet and fuse, and they must accordingly be regarded as belonging to both cells. Between these intercellular bridges there exists a system of channels which is in communication with the lymphatic system of the corium. These prickles are regarded by some as portoplasmic processes of the

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cells and by others as derived from cell membranes. Ranvier[35] has shown that the fibrillae may extend from one cell around several others before reaching their ultimate destination in other cells at some distance.

The *stratum corneum* forms the outer layer of the epidermis and presents a somewhat differentiated lower stratum, the *stratum lucidum*. This is transparent, containing a homogeneous substance which is probably derived from the more solid keratohyalin. The cells of the *stratum corneum* are flattened and cornified. In the interior of each cell a more or less degenerated nucleus may be seen but otherwise the contents are homogeneous. The remains of the prickles are occasionally seen.

The constant loss to which the epidermis is subjected by desquamation is compensated by a continuous upward pushing of its basal elements. New cells, being continually produced before the formation of the others has been quite completed, are removed in layers further and further from the surface of the corium. The cells assume, in turn, the characteristics of the layers through which they pass, appearing finally as elements of the *stratum corneum* and sharing in the ultimate fate of that layer. The corium is composed of fasciculi of connective tissue, closely interwoven and matted and containing bundles of smooth muscle fibers. The corium consists of two layers—of a deeper, loose, reticular layer and of a superficial, condensed, papillary layer supporting the papillae. The transition from one to the other is very gradual. Elastic fibers are present in both layers.

The recticular layer is made of a network of bundles of connective tissue. Nearly all the strands have a direction parallel with the surface of the skin and are surrounded by a reticulum of coarse elastic fibers. In the papillary layer, just underneath the epidermis, the strands of connective tissue, as well as the elastic fibers, are finer and accordingly form a denser tissue. This layer supports the papillae[36] which are knob-like or conical elevations of still denser tissue ending in one or more points. We accordingly find simple and compound papillae. The papillae are of two kinds, vascular and tactile, and are regularly arranged in parallel series. They are most numerous in those parts of the skin especially destined for the exercise of touch.

The surface of the papillary layer is covered by a delicate

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membrane—the basement membrane. Most authors believe that the basal cells of the epidermis are simply cemented to this layer. Others believe the membrane is of a fibrillar nature, and that the epithelial cells are provided with short basilar processes which penetrate within the basement membrane and are met there by similar structures from connective tissue cells of the corium.

The subcutaneous layer contains strands of connective tissue, more or less vertical, containing elastic fibers and joining the reticular layer to the superficial fascia of the body. These strands, the *retinaculae cutis*, enclose in their meshes, masses of fatty tissue which form the *panniculus adiposus*. The latter varies in thickness in different parts of the body. The vertical cords of connective tissue are accompanied by blood vessels, nerves and excretory ducts of glands.

The glands of the skin are of two kinds—sweat glands and sebaceous glands. The sweat glands are distributed throughout the entire skin but are especially numerous in certain regions. They are deeply imbedded, passing even into the subcutaneous connective tissue where they are surrounded by fat cells. They are of the simple tubular type and their secreting portion is coiled. The excretory duct is nearly straight in its course through the corium and becomes spiral in its passage through the epidermis. In the corium the excretory duct is lined by short columnar cells, irregularly arranged in two layers. In the epidermis it has no other wall than that supplied by the several layers of epidermal cells through which it passes, although these cells are concentrically arranged around the lumen of the duct. The secretary portion of the sweat gland is lined by cuboidal or columnar cells, with fine granular protplasm, round or oval nuclei possessing one or two nucleoli. Smooth muscle fibres are found between the gland cells and the basement membrane.

The sebaceous glands are of the simple branched alveolar type and lie beside the hair follicle. Each hair is flanked by one or more glands. They are imbedded in the upper strata of the corium and present every degree of complexity. As a rule the sebaceous gland empties by a wide excretory duct into the upper third of the hair follicle. The walls of the duct also secrete sebum. The glands are surrounded by sheaths of connective tissue which cover the hair follicle at the same time. Inside the

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sheath is the *membrane propria* which is a continuation of the glassy membrane of the follicle. The basal strata of granular cells should be regarded as a continuation of the external root-sheath. The central cells have a distinctly different appearance. The nuclei are compressed, owing to the accumulation of fat globules, and finally become small and angular. In the secretion of sebum the cells are consumed and the sebum contains fat globules mixed with cellular debris. Sebaceous glands are met in all parts of the body and are especially numerous in those parts exposed to the influence of friction.

A cutaneous gland is found in the pig, somewhat resembling the sebaceous gland. It is situated in the inner and posterior portion of the knee and is from ¾ to 2 inches in length and from ¼ to ½ inch in width.

Hair[37] is distributed over almost the entire extent of the skin, varying however, in quantity and arrangement in different regions of the body. The visible portion of the hair is called the shaft, and that portion below the skin is the root. The lower portion resting upon the papilla is the bulb, the sheath encircling the root and bulb is the root-sheath, the entire structure being called the hair follicle.

There are three superimposed layers in a hair. The epidermis (cuticle) is a thin lamella of overlying, plate-like cells, most of which are not nucleated. Its elements are marked on the surface of the hair by shaded lines anastomosing to form a network. The epidermis belongs to the shaft and to a portion of the root. Near the bulb it is replaced by soft nucleated cells, which are arranged vertically.

The cortex[34 38] is composed of several strata of long flattened nucleated cells. Scattered between and within the cells are pigment granules. At the root, the cells become polyhedric, are filled with fluid and exhibit a perfectly distinct nucleus.

The medulla occupies a narrow irregular cavity in the center of the hair. It contains from two to four strata of polygonal nucleated pigmented cells, which, according to Kolliker, contain fat granules and air vesicles. Many hairs show no medulla and even in thick hairs it does not always extend the entire leigth of the hair.

The inner root sheath consists of three concentric layers:—

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First, of an outer single layer of clear nonnucleated cells, the layer of Henle; second, of a thick middle layer of nucleated cells containing keratohyalin, the layer of Huxle; and, third, of an inner cuticle bordering upon the hair.

The outer root-sheath is made up of elements of the Malpighian layer. We have prickle cells here surrounded by an outer columnar layer.

The hair follicle[39] is a narrow cavity, slightly contracted at its orifice and dilated at the bottom, where the hair papilla is placed It is a simple involution of the skin as its structure shows. It is composed of an outer looser layer of longitudinal fibrous bundles, of an inner, more compact layer of fibers encircling the follicle; and of an inner-most well developed basement membrane—the glassy membrane.

The papilla[40] is a small, conical, vascular and nervous prolongation rising into the hair bulb. It furnishes the hair with nutrition and the elements of growth.

In the horse, the bristly appendages known as horsehair should be distinguished from the hairs proper; the latter are fine and short, particularly in the regions where the skin is thin, and spread over the entire surface of the body in a continuous layer which is called the coat. The former are long and flowing, occupy the summit of the head, where the constitute the forelock; the upper border of the neck, where they form the mane; and cover the caudal appendage with a tuft—the tail. Some of these also form special organs on the free margin of the eye-lids, and are termed eye-lashes. The hairs of the tail are the longest and strongest in the body. These particular hairs also grow on the posterior aspect of the limbs, generally from about the knees and hocks to the hoofs; at the sesamoid bones they constitute a long tuft—the fetlock—which surrounds the horny growth called ergot. These foot-locks are peculiar to the horse, and vary in length and coarseness with the breed of the animal.

When the hair is fine, long, and wavy, it forms wool; and when it is straight and rigid as in the pig, it is known as bristles. In the ass and mule, the forelock and mane are rudimentary or absent, and the hair of the tail is limited to a small tuft at the extremity of the organ in the former animal; while in the latter it is much less abundant than in the horse. In the ox, these hairs

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are not present, except at the extremity of the tail, as with the ass.

The ordinary hair of the coat is soft and elastic, inclined in particular directions, and varies in length not only according to the regions of the body on which it grows, but also according to the season or climate. In the horse, the direction of the hair of the coat gives rise to curiously formed waves, lines, and circles, the most constant of which is on the forehead.

In the cow, the hair is frizzly on the forehead; on the posterior part of the thighs it has a particular direction, while on the outer side it passes downwards. From the posterior part of the mammae it ascends as high as the vulva; this characteristic disposition forms what the French have termed "ecussons," by which some have pretended to recognize the lactiferous qualities of the animal. In the sheep, real hair—not wool—is found on the lower part of the face, and on the extremities of the limbs. In the goat, the hairs of the beard are very long and compose a distinct tuft. This animal has also a fine down beneath the ordinary hair. In the pig, the bristles are very strong in the region of the back. In old animals they are usually bi-or-tri-funcated at their free extremity. There is also a fine soft hair on this animal. In the dog, the length, fineness, and consistency of the hair depends on the breed. In the cat, the hair in some breeds—as in the Angora—is remarkable for its length and softness. In none of these animals is there foot-lock.

The histological technic we adapted in our work on animal skins, is as follows:—

The skin is fixed with 5 per cent. formalin for twenty-four hours, and is then treated with the reagents as indicated below:—

| | |
|---|---|
| 80 per cent. alcohol | 8–12 hours |
| 95 per cent. alcohol | 8–12 hours |
| Absolute alcohol | 8–12 hours |
| Absolute alcohol | 8–12 hours |
| Absolute alcohol plus $CS_2$ (equal parts) | 2 hours |
| $CS_2$ plus paraffine at 37° C. (1 part $CS_2$ to 3 parts paraffine) | 8–12 hours |
| Paraffine No. 1 | 1 hour |
| Paraffine No. 2 | 1 hour |

These pieces were then imbedded, cut at ten microns and stained as follows:—

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HAEMOTOXYLIN-EOSIN STAIN.

| | |
|---|---|
| 1. Xylol | 2 minutes |
| 2. Xylol | 2 minutes |
| 3. Absolute alcohol | 2 minutes |
| 4. Absolute alcohol | 2 minutes |
| 5. Absolute alcohol | 2 minutes |
| 6. 80 per cent. alcohol | 1 minute |
| 7. Distilled water | 1 minute |
| 8. Delafield's haemotoxylin | 6–8 minutes |
| 9. Tap water | 15 minutes |
| 10. 80 per cent. alcohol | 2 minutes |
| 11. Eosin | 45–60 seconds |
| 12. 95 per cent. alcohol | 2 minutes |
| 13. 95 per cent. alcohol | 2 minutes |
| 14. 95 per cent. alcohol | 2 minutes |
| 15. Absolute alcohol | 2 minutes |
| 16. Carbo-xylol (1 part phenol to 3 parts xylol) | 30 seconds |
| 17. Xylol | 2 minutes |
| 18. Xylol | 2 minutes |

VAN GIESON STAIN.

| | |
|---|---|
| 1. Xylol | 2 minutes |
| 2. Xylol | 2 minutes |
| 3. Absolute alcohol | 2 minutes |
| 4. Absolute alcohol | 2 minutes |
| 5. Absolute alcohol | 2 minutes |
| 6. 80 per cent. alcohol | 1 minute |
| 7. Distilled water | 1 minute |
| 8. (Strong) Delafield's haemotoxylin | |
| 9. Tap water | 15 minutes |
| 10. Van Gieson solution | |
| 11. 95 per cent. alcohol | 2 minutes |
| 12. Absolute alcohol | 2 minutes |
| 13. Carbo-xylol | 30 seconds |
| 14. Xylol | 2 minutes |
| 15. Xylol | 2 minutes |

WEIGERT STAIN.

| | |
|---|---|
| 1. Xylol | 2 minutes |
| 2. Xylol | 2 minutes |
| 3. Absolute alcohol | 2 minutes |
| 4. Absolute alcohol | 2 minutes |
| 5. Absolute alcohol | 2 minutes |
| 6. 80 per cent. alcohol | 1 minute |
| 7. Weigert solution | |
| 8. 95 per cent. alcohol | 2 minutes |
| 9. Absolute alcohol | 2 minutes |
| 10. Carbo-xylol | 30 seconds |
| 11. Xylol | 2 minutes |
| 12. Xylol | 2 minutes |

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Sections of skin were cut at ten microns and were studied with the following lenses:—

No. 3 ocular and No. 3 objective— 82 magnifications.
No. 3 ocular and No. E objective—505 magnifications.

An examination of a series from the normal skin through the bate yielded very interesting and in most cases satisfactory pictures of the skin after a particular treatment. An exhaustive study of any one process and ultimately of all the processes involved in the transformation of skin to leather would appear to be the logical sequence to this work.

1. In a section of normal calf skin made from the shoulder, two general layers are found—an epithelial layer on the surface with a connective tissue layer beneath. The connective tissue has an upper more cellular papillary layer and is directly continuous with a deeper, more densely fibrillated portion. The epithelium is of the stratified squamous type in which we can identify the *stratum germinativum,* the *stratum granulosum* and the *stratum lucidum.* On the surface we find the *stratum corneum.* Extending into the corium are hair follicles resembling those found in human skin. Opening into the sides of the follicles we find one or two sebaceous glands in the vicinity of which an *erector pili* muscle is present. The hair follicles show the inner epithelial root sheath and an outer connective tissue sheath. The large blood vessels are found at the level of the bases of the hair papillae which are at the level of the looser papillary layer of the connective tissue. The elastic tissue is concentrated directly below the *statum germinativum* and presents a woven, basket like arrangement around the hair and root.

2. After soaking in water for 42 hours the corneous layer shows slight atrophy. The cell boundaries have disappeared, the entire layer presenting a smooth homogeneous appearance. The *stratum germinativum* is less acidophilic and vacuoles are found in the deeper cells. Vacuoles are also present in the papillary layer of the connective tissue which is paler and shows many large shrinkage spaces. The elastic tissue appears normal. The hair reacts slightly to the stain but is otherwise normal.

3. After liming for 24 hours we find the *stratum corneum* dissociating from the deeper layers. The cell boundaries of the

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latter are indistinct and the cells show cloudy cytoplasm with pale nuclei. The cells chiefly in the lower half of the *stratum germinativum* dissociate from one another and the entire layer, especially at the center, presents many large transversely elongated spaces. The connective tissue is less fibrillated, paler and has fewer nuclei, is more compact and shows large shrinkage spaces. The hairs are thin and stain poorly. The epithelium of the sheath is shrunken and shows cellular dissociation. Many follicles are devoid of hair. The sebacious glands are paler than are the normal. The elastic tissue does not stain well.

4. After liming for 66 hours the entire epithelium and most of the papillary layer are absent. The fibrillar structure of the connective tissue is lacking and the tissue presents a picture seen in hyaline degeneration. The hair follicles, when present, are lined by single layers of badly staining epithelium and the epithelial sheath is reduced to a few layers of disintegrated cells. The sebaceous glands stain poorly.

5. After 120 hours liming and subsequent unhairing, the entire epithelial layer is absent. The connective tissue stains poorly, the nuclei show no detail and the fibrillar structure is not definite. The entire layer shows indications of hyaline degeneration.

6. After bating, the corium alone is left with perhaps an occasional strand of elastic tissue. The shrinkage spaces are not as large as in sections three or four. The tissue shows a very faint fibrillar structure and stains poorly.

KID: 1. In the study of a section of dry kid skin taken from the butt, the skin was found to be reduced in thickness. Both layers of the connective tissue were found to be more compact, especially the papillary layer. The tissue lacks its characteristic fibrillation and is less acidophilic. The epithelium has desquamated except in the lower layers of the *stratum germinativum* which is shrunken and presents nuclei more deeply stained than normal. The hair shows irregular shrinkage spaces in the center of the shaft; the cortex and the cuticle not staining. The entire thickness of the follicle is considerably reduced; the cells stain poorly and an indication of Huxle's and Henle's layers may be noticed.

2. The skin, after soaking 4 days in water, shows many shrinkage spaces. The corneous layer is thin and shrunken, shows no cell boundaries and is practically separated from the under-

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lying layer. The *stratum germinativum* is thin, stains poorly and shows no cell boundaries. The connective tissue is aggregated into masses, some of which show the normal fibrillation. The sebacious glands are normal. The hair show many pigment granules. The epithelial cells of the inner root sheath are in some cases dissociated and in other instances are cloudy with the preservation of cell outlines. The outer root sheath is thin and slightly cloudy.

3. After 24 hours in lime and $Na_2S$, the entire section, especially in the reticular layer, is increased in thickness and the *stratum corneum* is separated from the underlying layers. The deeper layers of the epithelium are cloudy and stain poorly. Many shrinkage spaces in the reticular layer of the connective tissue are presented. The hair follicles appear almost normal except that the cells of the inner and outer root sheaths stain poorly.

4. After 7 days in lime water and $Na_2S$ there is a slight thickening of the skin, especially in the corium. The *stratum corneum* shows desquamation. The *stratum germinativum* is cloudy, stains poorly and the cell boundaries are not differentiated. The papillary layer of the corium shows many fine shrinkage spaces. The connective tissue is cloudy and presents a thick, swollen appearance and it is hard to demonstrate the fibrillar structure. The reticular layer also shows the same lack of fibrillation, is less acidophilic and presents numerous large shrinkage spaces. The hair is swollen and shows a large, faintly acidophilic, vacuolated medulla. The hair is separated from the follicle by large shrinkage spaces. The cells of the inner root sheath are swollen and pale and are dissociating from one another while the cells of the outer root sheath present an appearance similar to that shown by *stratum germinativum*.

5. Upon unhairing after 15 days in lime water and $Na_2S$ the epithelium is almost entirely absent. The papillary layer shows shrinkage spaces and while slightly cloudy retains its fibrillated appearance. The deeper layers show considerable shrinkage with a picture suggesting hyaline degeneration. The hair follicles are empty.

6. After bating, there is no epithelium present. The nuclei of the connective tissue have disappeared and the fiber bundles show

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a glassy appearance. The tissue is slightly paler than normal and the entire section shows numerous fine shrinkage spaces.

CARBETTA 1 and 2: In the study of cabretta skin the general description given above for the dry and soaked skins (kid slides 1 and 2) will illustrate the conditions noticed in these slides (cabretta 1 and 2). The skin is thicker than the kid.

3. After 24 hours in lime water and $Na_2S$, the skin is presented in a state of fairly good preservation. In places the *stratum corneum* is absent and elsewhere is reduced to a thin structureless layer separated from the tissue beneath. The *stratum germinativum* is thin and is intensely stained. The papillary layer of the connective tissue is practically normal while the reticular layer is thin and lacks the longitudinal fibrillations. The sebaceous glands are normal as are the hair follicles.

4. After 7 days in lime water and $Na_2S$, the general appearance of the slide, with the exception of the desquamation of the *stratum corneum* may be characterized as good. The general impression that one obtains of the connective tissue is that the abnormal, shriveled appearance is almost gone. The *stratum germinativum* is about three cell layers deep and is slightly cloudy. The papillary layer is pale and with the reticular layer shows few nuclei. The sebaceous glands are unchanged. The hair follicles and the inner and outer layers of the root sheaths are paler and less distinct.

5 and 6. For the general appearance of these slides, see slides 5 and 6 of the kid series.

Since sections cut from skin at arbitrary periods during soaking, liming and bating show splendid pictures of what actually happens to the several layers, it would seem that the extension of this work is indicated. Sections might be cut every two hours and the finer changes studied. What we have seen in gross is the desquamation first of the corneous layer, then of the lower layers of the epithelium, accompanied by the intense swelling of the connective tissue. During the later periods of liming, the latter appears to lose its fibrillation. The swollen appearance disappears after bating and at times it is difficult to differentiate between the papillary and reticular layers.

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## SUMMARY.

1. Histological studies were made of calf, kid and cabretta skins.

2. Histological studies were made of the changes effected in the structures of calf, kid and cabretta skins, during soaking, liming and bating.

## CONCLUSIONS

1. Skin taken from several parts of the body varies in composition.

2. There is more mucoid in the butt than in the other parts.

3. There is a loss of cellular material during soaking, liming and bating. This is shown by the increase of coagulable protein and of metaphotein.

4. Elastin is digested in bating.

5. Water is absorbed in soaking and during the early periods of liming. In the latter periods of liming and bating there is a gradual loss of water.

6. In soaking, the corneous layer begins to desquamate. The lower layers of the epithelium and the connective tissue are swollen.

7. In liming, the corneous layer disappears; the lower layers of the epithelium show indistinct cell boundaries and transverse shrinkage spaces. They finally dissociate from the papillary layer. The connective tissue is less fibrillated, presents large shrinkage spaces and sometimes shows a picture seen in hyaline degeneration.

8. After bating, the connective tissue alone is left. The shinkage spaces are not so large as those seen in liming. The tissue also shows a faint fibrillar structure but stains poorly.

The author wishes to thank Professor William J. Gies for his kind help, friendly advice and constructive criticism generously offered during the course of this research.

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## TOTAL SULPHATES IN LEATHER.

*By Dr. L. E. Levi and Aug. C. Orthmann.*

In a former article we mentioned the fact that we had some 2,000 odd leather analyses to make during the year. It is but natural that the most rapid and accurate methods be used in order to clear the way for other work.

We have found it highly essential to make the total sulphate determination in all leathers finished or unfinished, that have been tanned with a chrome sulphate compound. This determination in conjunction with the chromium content will readily show the absence or presence of free sulphuric acid in the leather.

Where a basic chrome sulphate liquor has been used for tanning and the basicity further reduced by subsequent addition of alkali carbonates or hydrates after the leather has been chrome tanned, to further set the chrome, and after thorough washing with water, free sulphuric cannot be present. The sulphuric acid found in such a case would be combined with chromium, aluminum, iron, calcium, sodium and potassium, the last two are entirely removed on proper washing, thus by determining the chromium and the sulphates, and calculating the latter to $H_2SO_4$, the proportion of one to the other will determine the chrome compound present, due allowance must be made for acid combined with aluminum, iron and calcium.

Normal chromium sulphate ($Cr_2(SO_4)_3$) is a combination of 38.78 per cent. $Cr_2O_3$ and 61.22 per cent. $SO_3$ and if this proportion exceeds these figures it is a sure sign that free acid is present.

Realizing the importance of this determination in that the basicity of leather could be easily controlled, the matter of selecting a rapid and accurate method for the same suggested itself. The bomb method, the nitric acid method and the method of Balland and Maljean have been used in this laboratory up to the year 1914. These methods, however accurate, were found wanting regarding rapidity, neither of which could in any way be improved upon in this respect. The bomb method; an Emerson calorimeter bomb was used for this purpose, 1 gram of leather

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was placed in a platinum shell which in turn was placed in the bomb, the lower part of the bomb was covered with sodium carbonate, then filled with oxygen at a pressure of about 25 atmospheres and ignited by means of an electric current and iron wire, the released gases were led into a beaker containing N/10 alkali and the solid contents of the bomb were washed into this beaker with hot water, the whole acidified, boiled and filtered, the filtrate boiled and treated with $BaCl_2$.

The nitric acid method of Wuensch and the sodium carbonate method of Balland and Maljean were carried out as given in Procter's Leather Industries Laboratory book, 2nd edition, pp. 370 and 371.

The method we finally adopted, is as accurate as any of the above and at the same time more rapid than any of them. Chromic acid strongly acidified with hydrochloric acid is used to oxidize the organic matter and any chromic acid not reduced in this way is reduced by means of alcohol, the remaining alcohol and resulting aldehyde are boiled off. The method is carried out as follows:—

*The Reagent.*—Take 50 grams of chemically pure potassium bichromate and dissolve in 150 cc. of water; when dissolved add 50 cc. of chemically pure concentrated hydrochloric acid. Weigh out 1 gram of the fat free leather into a 250 cc. beaker and add 20 cc. of the reagent and bring to a gentle boil then add 8 to 10 cc. of hydrochloric acid, let digest over burner until all organic matter is destroyed. Then boil vigorously for 2 or 3 minutes after which add about 50 cc. water and about 5 cc. of alcohol, boil until all chrome is reduced and alcohol and aldehyde is driven off then add 50 cc. more water bring to a boil and add barium chloride solution, let stand 2 or 3 hours, filter and wash precipitate and burn as usual.

In case a leather contains talc or allied substance filtration must take place before adding barium cholride.

A comparison of the different methods follows. One gram of finely divided fat free leather was used.

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| | Weight $BaSO_4$ grams | Calculated to per cent. $H_2SO_4$ |
|---|---|---|
| Bomb method | 0.1032 | 4.3375 |
| | 0.1020 | 4.2870 |
| Wuensch's nitric acid method | 0.1034 | 4.3459 |
| | 0.1017 | 4.2744 |
| Balland and Maljean sodium carbonate method | 0.1024 | 4.3039 |
| | 0.1032 | 4.3375 |
| Chromic acid method | 0.1012 | 4.2534 |
| | 0.1015 | 4.2660 |

In articles published by the authors (this JOURNAL, July, 1914, and September, 1915), we had the pleasure of giving to the Leather Chemists methods as used in our laboratory with the hope that all other members of our association would give our members the benefit of their knowledge and experience of the various methods used by them in their laboratories so as to bring us one step nearer to the realization of that goal to which we are all striving, namely, the standardization of methods. We are very sorry to say that our hopes have been almost blasted. We say almost blasted because we think the bright light of the aurora of uniform methods will penetrate the dark recesses of inactivity and awaken our fellow chemists to give for the benefit of all their most valuable experiences and thereby brighten the field of uniformity.

Laboratory of the Pfister and Vogel Leather Co.,
Milwaukee, Wis., July, 1916.

## THE WEAR RESISTANCE OF SOLE LEATHERS, II.

*By Lloyd Balderston.*

In making the test mentioned in the previous paper (see next preceding number, this JOURNAL), the number of teeth on the gear attached to the wear wheel was 62 and in the case of the sample wheel 78. (There was no reason for choosing these particular numbers. In this and previous experiments gears were used which happened to be on hand.) The amount of friction seemed rather too large, so a new gear with 70 teeth was made to replace the 62-tooth wheel, making the ratio of rates 35 to 39, or 0.8974, nearly 0.9. The extent of rub on each piece is therefore about $0.9 \times 1.1$, or one-tenth of an inch, nearly.

The driving pulley was also changed, being reduced from 12

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inches to 7 inches, thus increasing the speed so as to reduce the time for 50,000 revolutions from 30 hours to about 16 hours.

The plan of weighing the samples mentioned in the previous paper (putting the samples together with the check pieces in an air-tight vessel for one or two days before weighing) was tried, with satisfactory results. Losses as estimated by weighings on successive days agreed within two or three milligrams.

With a view to testing the statement made by Mr. J. H. Yocum in regard to the relative wearing qualities of the grain side and flesh side of sole leather,[2] four samples of each of five kinds of leather were included in the first run with the revised apparatus, two with the grain side out and two with the flesh side out. Four pieces of the same leather substitute mentioned in the former paper were included in the set. The English sample is an imitation hemlock, colored red with an oil-soluble dye. The pieces were run 50,000 revolutions, at 40 pounds pressure. Results are given in the table.

| Kind of leather | New wt. grams | Worn wt. grams | Loss grams | Corrected loss grams | Loss per cent. | Average per cent. loss |
|---|---|---|---|---|---|---|
| Scoured Oak: | | | | | | |
| Flesh out ..... | 4.535 | 4.079 | 0.456 | 0.444 | 9.8 | |
| | 4.345 | 3.929 | 0.416 | 0.404 | 9.3 | 9.5 |
| Grain out ..... | 4.553 | 4.273 | 0.280 | 0.268 | 5.8 | |
| | 4.511 | 4.228 | 0.283 | 0.271 | 6.2 | 6.0 |
| English Red: | | | | | | |
| Flesh out ..... | 4.955 | 4.286 | 0.669 | 0.651 | 13.1 | |
| | 4.927 | 4.425 | 0.502 | 0.484 | 9.8 | 11.5 |
| Grain out ..... | 5.161 | 4.610 | 0.551 | 0.533 | 10.3 | |
| | 4.876 | 4.420 | 0.456 | 0.438 | 9.0 | 9.6 |
| Texas Oak: | | | | | | |
| Flesh out ..... | 4.259 | 3.595 | 0.664 | 0.649 | 15.2 | |
| | 4.171 | 3.545 | 0.626 | 0.611 | 14.6 | 14.9 |
| Grain out ..... | 4.398 | 4.115 | 0.283 | 0.268 | 6.2 | |
| | 4.346 | 4.020 | 0.326 | 0.311 | 7.2 | 6.7 |
| Union: | | | | | | |
| Flesh out ..... | 4.346 | 3.798 | 0.548 | 0.534 | 12.3 | |
| | 4.405 | 3.864 | 0.541 | 0.527 | 12.0 | 12.1 |
| Grain out ..... | 4.344 | 4.124 | 0.220 | 0.206 | 4.7 | |
| | 4.343 | 4.038 | 0.305 | 0.291 | 6.7 | 5.7 |
| Hemlock: | | | | | | |
| Flesh out ..... | 4.143 | 3.473 | 0.670 | 0.656 | 15.8 | |
| | 4.185 | 3.603 | 0.582 | 0.568 | 13.5 | 14.7 |
| Grain out ..... | 4.410 | 3.994 | 0.416 | 0.402 | 9.1 | |
| | 4.268 | 3.847 | 0.421 | 0.407 | 9.5 | 9.3 |
| Leather Substitute: | 5.380 | 4.312 | 1.068 | 1.068 | 19.8 | |
| | 5.333 | 4.323 | 1.010 | 1.010 | 19.0 | |
| | 5.320 | 4.372 | 0.948 | 0.948 | 17.9 | |
| | 5.143 | 4.628 | 0.515 | 0.515 | 10.0 | |

[1] Page 439, August issue.

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In the matter of concordance, these results leave much to be desired. The order of contact with the wearing surface is given by reading up the columns. The reason for the last sample in the column showing so much less wear than the others of the same material is evidently because the oak leather which preceded it held the wheels apart so that the first piece of the substitute to strike the wear surface was worn into a wedge, sloping away from the leather. In order to avoid the special stress due to sudden changes of thickness it will probably be necessary to use as many as six samples of each kind and to reject the first and last piece of each series.

In spite of the lack of concordance in results, it is sufficiently evident that in the case of these samples the flesh side does not wear better than the grain. All but one of the kinds of leather show so much better results for the grain side that the difference can hardly be accidental or non-significant.

Elk Tanning Co. Laboratory,
Ridgway, Pa.

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## THE ACIDITY OF TANNERY LIQUORS.*

*By Hugh Garner Bennett, M.Sc., F.C.S.*

Another attempt is here made to solve the problem of the acidity of tan liquors. The starting point of this attempt is the recognition that these liquors contain a very complex mixture of weak acids, and that for their estimation it is necessary in the first instance to classify them according to type, *i. e.,* to separate them into groups which have definite differences from other groups.

One of these groups must obviously be the "tannins" or "tannic acids." These, though differing widely in many respects, are a fairly definite group of compounds, of which the most characteristic properties are their capacity for making hide into leather, and of giving a precipitate with a 1 per cent. gelatin, 10 per cent. salt solution. The tannins are weak acids, but in nearly all liquors they form much the largest proportion of the total acids present. It is important to bear this in mind, as it is a fact

* *Collegium*, London Edition, May 1916, pp. 106–113.

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which has been unrealized or ignored by some experimenters on this question.

The volatile acids of tan liquors are also a fairly definite group. Their volatility may be taken as the distinguishing feature, but they are also substances of well known constitution, *e. g.*, acetic acid. Next to the tannins, they form the largest proportion of the mixture, and are almost as important from a practical standpoint.

The rest of the acids in the tan liquor mixture may be defined negatively as non-tannin and non-volatile acids Gallic acid is the typical example of this class.

It must be borne in mind that all these acids are very weak. Hence, if it be desired to estimate their amount by titration, phenolphthalein is practically the only suitable indicator. Turmeric paper is the only conceivable alternative, and in that case boric acid must be certainly absent. If the tan liquor be titrated with N/10 caustic soda and phenolphthalein, the total acidity of the liquor may be determined with an accuracy which is really better than appears from the end point. Various suggestions have been made to improve this end point, but none have much effect. There are the alternatives of titrating the concentrated liquor and spotting on phenolphthalein paper, or of titrating the diluted liquor with phenolphthalein as internal indicator, and multiplying up the result according to the dilution. In the first case the results are not very concordant; in the second case a small error is magnified. Both methods give about the same results, but the author much prefers the second on the ground of better concordance. The accuracy is not of the highest order, but it is better frankly to recognize the limitations of the method than to strive after a delusive precision. The mode of procedure invariably adopted by the writer is to titrate 10 cc. of the liquor as diluted for analysis with N/10 caustic soda and phenolphthalein as internal indicato, until the red color appears distinctly. The result is then calculated to 10 cc. of the original liquor.

As a mixture of acids is being dealt with, it is futile to attempt the expression of results in percentages. It is both simpler and more significant to state acidities as the number of cubic centimeters N/10 caustic soda required for 10 cc. of tan liquor.

The methods for distinguishing the three groups of acids must

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now be considered. The weakness of every acidity method yet suggested is that this distinction has been either imperfect or unrecognized. All the useful information these methods supply, can be supplied more accurately by an ordinary hide powder analysis. Most of them yield results which are roughly proportional to the percentage of soluble solids, and if,—to throw light upon their divergence from strict proportion—these acidities be calculated as "acidity per unit of soluble solid," it will then be seen that they vary roughly with the percentage of non-tannins. There is no practical value in such rough determination of tannin and non-tans when their amounts can be obtained as quickly and more accurately by the usual gravimetric process.

A qualifying word of praise is due to the lime water method. When applied to the weakest liquors of the yard it does measure exactly the acids capable of forming soluble salts with lime, which determination has in these liquors, a distinct practical value.

The lead oxide method, involving detannization, gives results which are roughly proportional to the percentage of non-tans, and has been discarded for that reason.

The gelatin method, involving detannization with gelatin, gives (when carried out carefully under the best conditions) results which are still approximately proportional to the percentage of soluble solids! This fact makes it perhaps the most futile of all methods. If it be carried out under conditions not the best, *e. g.*, varying proportions of gelatin and tannin, and varying dilutions, then its results are without the faintest significance of any kind.

The writer is of the opinion that much the best method of distinguishing between the tannins and the non-volatile non-tans, is the hide powder process. That indeed is why the process is in common use. From the acidity point of view this process has been neglected because the hide powder readily absorbs an indefinite amount of the volatile acids. For example, if one titrates the ordinary non-tan filtrates in the official method of tannin analysis, what is determined is the unabsorbed volatile acids *plus* the non-volatile non-tannin acids. If, however, the liquors are analyzed by the method recently suggested by the writer (*J. S. C. I.*, 1914, 1184), a solution of the question appears.

In the first place the tannic acids and the non-volatile non-tannin acids are distinguished much more accurately than by any

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method yet suggested. In addition, by evaporating in the presence of an excess of tartaric acid, all the volatile acids—free and combined—may be completely expelled from both the soluble solids and the non-tans. The residues of soluble solids and non-tans may be re-dissolved, titrated with caustic soda, and these results, together with a determination of the total acidity, supply three equations to calculate the three unknown factors required.

It is suggested, therefore, that the acidity of tannery liquors should be carried out as follows:—

The tan liquor is filtered and diluted to contain 0.2 per cent. tannin approximately. Detannization by the revised shake method as suggested for tannery liquors is then carried out. The acidities are then determined thus:—

(1.) Ten cubic centimeters diluted liquor are titrated with N/10 caustic soda, using 5 drops 1 per cent. phenolphthalein as internal indicator.

(2.) Ten cubic centimeters diluted liquor are evaporated to dryness in the presence of 5 cc. of a 0.5 per cent. tartaric acid solution and heated for one hour in the steam oven. The residue is then re-dissolved in a little distilled water and titrated with N/10 caustic soda, as before.

(3.) Eleven cubic centimeters non-tan filtrate is similarly evaporated to dryness in the presence of 5 cc. of 0.5 per cent. tartaric acid solution, the residue dried for one hour, re-dissolved and titrated with N/10 caustic soda.

The amount of alkali required by the tartaric acid should be deducted from the 2nd and 3rd titrations. Each of these results is then multiplied by the dilution, and stated as the number of cubic centimeters N/10 caustic soda required for 10 cc. of the original liquor.

The first titration gives the "total acidity" of the liquor. The second titration gives what may be called the "soluble solid acidity" of the liquor, and the third titration yields the "non-volatile non-tannin acidity" of the liquor. The last is one of the factors required. It is obvious that the "tannin acidity," *i. e.*, the acidity of the liquor due to tannin, will be obtained by subtracting this non-volatile non-tannin acidity from the soluble solid acidity. Similarly the "volatile acidity," *i. e.*, the acidity of the

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liquor due to volatile acids, will be obtained by subtracting the soluble solid acidity from the total acidity. The acidity of any liquor may then be stated thus:—

| | cc. N/10 NaOH required by 10 cc. liquor |
|---|---|
| Tannin acidity | $= a$ |
| Volatile acidity | $= b$ |
| Non-volatile non-tannin acidity | $= c$ |
| Total acidity | $n$ |

Acidity determinations by this method in the writer's laboratory have yielded interesting results. One point which claimed immediate attention was that in all infusions of tanning materials there are bases present as well as acids. Such infusions and liquors almost invariably contain the salts of the various acids in addition to the free acids themselves. It is of course impossible definitely to assign these bases to any acid or group of acids. The fact that both acids and salts are ionized renders any such grouping quite arbitrary. Nevertheless, it is convenient to make some assumption of this kind, just as one must do in the analysis of a mixture of inorganic salts. This may be justified also to some extent by looking at the matter from the practical standpoint of what would happen if the liquor had some pelt put into it. To take a simple but fairly typical case, a 7 per cent. solution of gallo-tannic acid containing a little gallic acid and a little calcium acetate may be considered. If pelt were placed in this liquor, there is little doubt it would exhibit a preferential absorption of gallo-tannic and acetic acid, tending thereby to leave calcium gallate in solution. The method of determining acidities, as suggested above, also points to the convenience of making the same assumption, *viz.*, that any bases which are present should be grouped along with the non-volatile non-tannin acids, such as gallic, succinic, etc.

The titration of the residues from the non-tan filtrates really measures the non-volatile acids *minus* the bases present. The author was rather surprised to find that in nearly all tanning materials, and in most of the strong and "sweet" liquors of the tanyard, the bases present are more than sufficient to neutralize all the non-volatile non-tannin acids. The non-volatile non-tannin acidity turns out to be a negative quantity! Moreover, in

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liquors fresh from the leaches and in fresh laboratory infusions of some materials, the author has found that the volatile acidity (positive) was often exactly equal to the non-volatile non-tannin acidity (negative). These seem to point very strongly to the conclusion that a fresh infusion of tanning material leaches out the tannin and neutral salts of volatile acids.

EXAMPLE 1.

| | cc. N/10 soda per 10 cc. original liquor |
|---|---|
| 1st titration (total acidity) | = + 63.2 |
| 2nd titration (soluble solid acidity | = + 50.6 |
| 3rd titration (on-volatile non-tannin acidity | = — 12.6 |

Hence, volatile acidity = + 12.6 { No. 1, minus No. 2. }
and tannin acidity = 50.6 —(— 12.6) { No. 1, minus No. 3. }
= 63.2

Now it would be somewhat absurd to record in analysis a negative acidity, so that it is necessary if there be any bases present over and above the quantity required to neutralize the non-volatile non-tannin acids, to assume that they neutralize the volatile acids. Hence, where a negative non-volatile acidity is found, this quantity should be deducted from the volatile acidity. In such a case the non-volatile non-tannin acidity is of course always nil. The results obtained in the above example would then be reported as follows:—

| | cc. N/10 NaOH per 10 cc. liquor |
|---|---|
| Tannin acidity | = 63.2 |
| Free volatile acidity | = 0.0 |
| Non-volalile non-tannin acidity | = 0.0 |
| Total acidity | 63.2 |

EXAMPLE 2.—For further illustration take a handler liquor of 66° Barkometer, which has been worked down the yard in the usual way.

| | |
|---|---|
| 1st titration (total acidity) | = + 42.8 |
| 2nd titration (soluble solid acidity) | = + 25.0 |
| 3rd titration non-volatile non-tannin acidity | = — 1.8 |

Hence, tannin acidity .... = 26.8
and volatile acidity .... = (42.8 — 25 ) = 17.8
and free volatile acidity = (17.8 — 1.8) = 16.0

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The liquor would therefore be reported thus:—

| | cc. N/10 NaOH per 10 cc. liquor |
|---|---|
| Tannin acidity | = 26.8 |
| Free volatile acidity | = 16.0 |
| Non-volatile non-tannin acidity | = 0.0 |
| Total acidity | 42.8 |

EXAMPLE 3.—A further case may be given of a liquor of 41° Barkometer, worked still further down the yard. In this case the non-volatile non-tannin acids are more than sufficient to neutralize the bases present.

| | |
|---|---|
| 1st titration (total acidity) | = 19.4 |
| 2nd titration (soluble solids acidity) | = 11.9 |
| 3rd titration (non-volatile non-tannin acidity) | = 2.5 |
| Hence, tannin acidity = (11.9 — 2.5) | = 9.4 |
| and volatile acidity = (19.4 — 11.9) | = 7.5 |

The liquor would therefore be reported thus:—

| | cc. N/10 NaOH per 10 cc. liquor |
|---|---|
| Tannin acidity | = 9.4 |
| Volatile acidity | = 7.5 |
| Non-volatile non-tannin acidity | = 2.5 |
| Total acidity | 19.4 |

The bases present in tan liquors seem to originate from various sources. Some (as shown above) are leached out of the tanning materials as salts of volatile acid; some may be derived from the hardness of the water; some come forward with the goods from the limeyard. It seems necessary to introduce the conception of the "basicity of a tan liquor." This may be defined as the number of cubic centimeters N/10 acid required to neutralize the bases in 10 cc. of tan liquor. Assuming the bases are all inorganic, the basicity of a tan liquor may be determined as follows:—

Ten cubic centimeters of the diluted liquor (0.2 per cent. tan) are evaporated to dryness in a platinum basin and then ignited strongly and allowed to cool. In this way the bases are obtained as a white ash. Their amount is then readily determined indirectly as follows: To the ash is pipetted 5 cc. of a 0.5 per cent. solution of tartaric acid. This is then evaporated to dryness, dissolved up, washed into a conical flask and titrated with phenolphthalein and N/10 caustic soda. If $x$ cc. are required then

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$(3.2 - x)$ cc. is the amount of N/10 acid equivalent to the bases in 10 cc. of diluted liquor. The end point is sharp in this case as no organic matters are concerned. The result is then calculated to the original liquor.

The author has some evidence that the assumption that all the bases are inorganic is not altogether justified, for the basicity of liquors as determined above is sometimes less than the negative value of the non-volatile non-tannin acidity. From this one must conclude either that organic bases are present, or that compounds such as ammonium salts are present and driven off during the ignition. This latter alternative is indeed very probable, for ammonia is known to come forward with limed goods. The determination of the total basicity of a tan liquor is thus a problem not yet completely solved. The inorganic basicity is, however, a useful determination in green liquors.

Another point of great practical importance is the *relative* concentrations of the tannic acids and the volatile acids. There is no doubt that the relative proportions of these acids is a matter of first importance in determining the quality of the leather. The author suggests that the conception of a "volatile acid ratio" would be of practical value. This might be defined as the volatile acidity per unit of tannin acidity. The non-volatile acid ratio would similarly be the amount of non-volatile non-tannin acids per unit tan. To take the same three liquors as above by way of illustration, we should obtain:—

| | Volatile acid ratio | Non-volatile acid ratio |
|---|---|---|
| 100° liquor | nil | nil |
| 66° liquor | 0.60 | nil |
| 41° liquor | 0.80 | 0.27 |

This method of acidity determination has also yielded an interesting significance when taken in conjunction with the ordinary analysis of the liquor. It is clear that in the case of the soluble solids, the non-tans and the tannin, there are substances which can not only be weighed but also titrated, and by connecting these figures we can obtain what is practically a chemical equivalent of these bodies. It is true that mixtures are being dealt with, but that does not prevent the results from being characteristic of the materials in question. The case is strictly analogous to the de-

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termination of "acid values" of oils and fats, and it is proposed to apply a similar concept to tanning materials and tan liquors. "Tannic acid values" and "non-tannin acid values" will thus be obtained, which may be defined in a manner analogous to that of oils. The acid value of an oil is defined as the number of milligrams caustic potash (KOH) required to neutralize the free acids in 1 gram of oil. The case of tanning materials on account of the bad end point in titration, does not offer the same degree of accuracy, so that centigrams must be substituted for milligrams. It is also suggested that for tanning materials caustic soda be taken instead of caustic potash, partly on the ground that most chemists actually use it, and partly because its molecular weight is 40 and the calculations are simplified in consequence. The definitions will therefore be as follows:—

*The soluble solid acid value* of a tanning material is the number of centigrams caustic soda (NaOH) required to neutralize one gram of the soluble solids of that material.

*The non-tannin acid value* of a tanning material is the number of centigrams caustic soda required to neutralize one gram of the non-tannins of that material.

*The tannic acid value* of tanning material is the number of centigrams of caustic soda required to neutralize one gram of the tannin of that material.

It will be noticed that these acid values are calculated to one gram of tan, non-tan, etc., and consequently the same definitions are equally applicable to tan liquors and tanning material. The results then are quite comparable. As the weight of volatile acids is not known, the "volatile acid value" cannot be calculated. There is, however, no serious loss thereby, as these acids are of familiar constitution.

Determinations of the acid values of the different tannins, and of the non-tans associated with them, have been made. The materials were analyzed by the improved shake method recently suggested by the writer (*J. S. C. I.*, 1914, 1184), and the acidities of the non-tans and tannins determined as suggested in this article. From these two sets of figures the acid values were calculated.

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| Material | Tannic acid value | Non-tannin acid value |
|---|---|---|
| Sumac | + 15 to + 18 | — 5 to — 8 |
| Chestnut | + 15 | — 9 |
| Myrobalans | + 18 | — 11 |
| Myrobalans extract | + 20 to + 15 | — 5 to —9 |
| Quebracho | + 5 | — 14 |
| Mimosa | + 2 | + 4 |
| Cube Gambier | + 15 | — 7 |
| Block gambier | + 13 | — 5 |
| Gallo-tannic acid | + 9 | —— |
| Gallic acid | —— | + 2.58 |

It will be seen that the tannic acid values vary from 2 to 25, a range which is certainly much wider than the experimental error. It was hoped that some light might be thrown upon the constitution of pyrogallol and catechol tannins, but the differences are not striking. Nevertheless, these figures seem to be typical of the various materials, in the same sense as a saponification value of an oil.

It will be noticed that the non-tannin acid values are nearly all negative. This of course results from the negative non-tannin acidities which have been explained above. In this case also there is considerable range of variation—from +4 to —11. In the case of the non-tans also this experimental error is small, for the percentage of non-tans can easily be determined to ¼ per cent., and the titration of the residues gives a much better end point than when tannin is present. These negative results indicate the presence of volatile acids, and of bases in practically all tanning materials, and show clearly that it would be advantageous to use tartaric acid, in the manner suggested by the author, not only in the analysis of tan liquors (as previously suggested) but in the analysis of tanning materials and tanning extracts also. In the present official procedure, both the soluble solids and the non-tannin residues contain alkali, which fact cannot be conducive either to concordance or correctness. Moreover, from the standpoint either of tannin estimations or of acid estimations, it seems highly desirable to reduce the proportion of hide powder to the very minimum. This will tend not only to accuracy, but to concordance also, because all determinations will then be less dependent upon variations in the quality of the hide powder.

In conclusion, it may be pointed out that the determination of the acidity of tan liquors, as here suggested, involves little manip-

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ulative labor if taken in conjunction with the hide powder analysis. The two processes may be fused. If the residues of soluble solids and non-tans be weighed before dissolving for titration, that is all the extra labor required for the complete analysis.

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## DISINFECTION OF TANNERIES.

The following letter from the chief of the Quarantine Division, Bureau of Animal Industry, is of interest to tanners and chemists alike:

UNITED STATES DEPARTMENT OF AGRICULTURE.

*Bureau of Animal Industry.*

Washington, D. C., July 18, 1916.

MR. CUDWORTH BEYE, Executive Secretary,
The National Association of Tanners,
146 Summer St., Boston, Mass.

DEAR SIR:

This will acknowledge receipt of your letter of July 16, requesting suggestions for the disinfection of the premises of tanneries for the purpose of getting rid of anthrax infection. You are advised that next to fire, bichloride of mercury appears to be the most efficient agent in the sterilization of the anthrax spore.

It would be dangerous to scrape and sweep the various parts, such as walls, ceilings, joists, woodwork, floors, etc., when dry, and thus raise a dust. Therefore, all parts of the buildings or structures which may be infected should be thoroughly sprayed and wetted with the bichloride of mercury solution of the strength of 1 to 1,000. The debris could then be gathered up and burned under the boiler or otherwise with the aid of kerosene. Then all parts of the building or premises should be scrubbed with the bichloride of mercury solution, scrubbing to be followed by another spraying or hosing of all parts, which should then be permitted to dry. Under these conditions, there would be three applications of the bichloride of mercury solution which should in each instance be used in the proportion of 1 part of the bichloride to 1,000 parts of water.

On account of the poisonous nature of bichloride of mercury,

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care must be exercised to prevent mercurial poisoning of those employed in its use. Continuous wetting of the hands with it, getting other parts of the body wet with the solution, or keeping it in contact with the skin for considerable periods of time should be avoided.

Very truly yours,
(Signed) R. W. HICKMAN,
*Chief, Quarantine Division.*

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## ABSTRACTS.

**The Work of the Imperial Institute for India.** WYNDHAM DUNSTAN, Director. *Journal of the Royal Society of Arts,* Vol. 64, pp. 593-604. The Institute has been in existence for more than 20 years, and has been a Government institution for 13 years. It has carried on many scientific and technical researches with a view to the further development of the resources of India, and maintains museums in which Indian products are on exhibition. The principal exhibits are in the Indian Section of the South Kensington Museum, London. The number of visitors to the Section reaches 250,000 annually. Several research laboratories are maintained at South Kensington, and one at the Forest Research Institute at Dehra Dun, India. (Contributions from the Forest Research Institute over the name of Puran Singh appear from time to time in the *Journal of the Society of Chemical Industry,* and a number of these have been reprinted in this JOURNAL.—ED.) In general, the results of researches are published in the *Bulletin of the Imperial Institute.* The Institute aims to further the utilization in India of its own natural resources, a large part of which are now exported in a raw state. This applies to leather materials especially. India produces large quantities of tanning materials and also of hides and skins, but little leather is tanned in the country. The section of Professor Dunstan's paper on this subject is as follows:

> There have been made at the Imperial Institute a large number of investigations of the value of Indian tanning materials, with a view to the exportation to Great Britain of those which are rich in tannin, but were not known or used by the British tanner, and to the utilization of those (such as the barks of cassias, acacias, shorea and mangrove) which are too poor to repay export in the crude state. Some of these, however, might be profitably manufactured into extracts in India, and partly utilized there and partly exported for tanning purposes in Great Britain. This work has involved not merely investigation of the constituents of the materials, but technical trials in connection with tanners.
>
> Much of this work has been done in co-operation with the Forest Department and with the Forest Research Institute at Dehra

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Dun. After many years' work some progress has been made, and the manufacture of extracts from these materials is about to be tried systematically. There is great opening for the development of tanning extract manufacture and of tanning industry in India, including the extension of native tanneries. The supply of suitable hides and skins is enormous, and a large part of these which have hitherto been exported, chiefly to Germany, should in future be tanned in India. No doubt in some instances chemical or chrome tannage could be adopted with advantage, but vegetable tannage should remain an important Indian industry and receive development along scientific lines. A definite scheme of operations is required, in connection with which the needs of Indian tanners and those of British purchasers should be taken into account.

Among the unutilized vegetable tanning agents of India which have been investigated at the Imperial Institute is *Caesalpinia digyna,* a common plant in many districts of Assam and Burma. Investigations at the Imperial Institute have shown that the shells or cases of the seed pods of this plant contain about 60 per cent. of tannin. Technical trials as a tanning agent on a small scale showed that the material produced excellent leather, and this conclusion has been confirmed by trials on a large scale in the tan-yard. A demand in consequence arose for the material in Great Britain, but so far the supply has been small. Whenever the pod-cases of *C. digyna* have been offered, they have been sold readily at good prices. It would appear that the cost of collecting and shelling pods from the wild plant will interfere with the extended use of this promising material, and that further progress can only be made through the cultivation of the plant in India, which is now under consideration. (For further information in regard to *Caesapinia digyna,* called Tari or Teri pods, and also Sunle-the, see paper by T. A. Faust, this JOURNAL, 1913, pp. 154-8, and notes from the *Bulletin of the Imperial Institute,* this JOURNAL, 1915, pp. 307-10.)

**Cuban Tannery to Install Modern Machinery.** *Commerce Report,* July 24, 1916. In the city of Santiago de Cuba there is only one tannery of any importance. Sole leather and harness leather are the types produced by this concern, the former being sent principally to Habana for use in the manufacture of cheap country shoes, and the latter being distributed to saddlery and harness makers all over the island.

Mangle bark is the chief tanning material used, an inexhaustible supply of this article being found on the shores and neighboring keys of the southern coast of Cuba. No machinery or chemicals are employed in the tanning process, and primitive methods are in use. After liming and drenching, the hides are softened in a composition of honey and water for 36 hours before entering the mangle vat. The proprietor is in the market for bark-crushing machinery and it is believed that gradually other modern tanning equipment will be installed in this tannery.

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**Experience of Tanning Company in China.** CONSUL GENERAL THOMAS SAMMONS, Shanghai, May 25. *Commerce Report.* Imports of various kinds of leather into China, amounting approximately to $4,000,000 annually, are sufficiently large to have caused tentative proposals to be made from time to time for the establishment of tanneries at Shanghai to meet local market demands. As the affairs of the Shanghai Tannery Co. are being liquidated, details of the undertaking from its inception may prove of value. The Shanghai Tannery Co. (Ltd.) was formed in 1906 with an authorized capital of 100,000 taels ($76,000). The paid-up capital was 70,000 taels ($53,200), with stock of 5,000 taels ($3,800) face value, presented to one of the persons interested as compensation for work in promoting the formation of the company and superintending the construction of the plant. At the outset, it was intended that the principal product should be sole and harness leather, but the limited amount of available working capital was inadequate to meet the requirements of the slow "pit" process that had been installed. Moreover, it is stated that too much of the available capital was laid out in the construction of the plant. The pits were constructed in the wrong proportions for the tanning of sole and harness leather. Some of the machines that were ordered were in excess of the requirements and were, in fact, never used. It is also stated that the quantity of leather produced did not justify an input of more than 200 hides a month, and the overhead charges were disproportionate to the production. The management of the tannery changed hands several times, but despite the changes the physical and financial conditions of the company grew steadily worse until, in 1909, some new capital was obtained and it was decided to enlarge the plant so as to enable it to use 600 hides a month. But during this year a fire of unknown origin badly damaged the tannery. The insurance company paid 75,000 taels ($57,000), and it was decided to rebuild. Operations were commenced immediately, and again the plant was ready for work. However, the company was soon deeply in debt. In 1914 a new tanning expert was secured, and he substituted the "drum" system for the antiquated "pit" process, shortening the time required for tanning from six or eight months to two months. The hides are kept in motion by means of a moving drum. The motion is said to cause them to absorb the tanning material much more rapidly. After this change in method the condition of the company improved. The book returns obtained by the "drum" system were quite satisfactory. It is said the tanning expert in charge at this time was using quebracho and chestnut extracts to the exclusion of all other material, and the leather obtained by this process was good in appearance and quality. In October, 1914, negotiations were commenced with the object of furnishing boots to the Russian Government. Subsequently the Shanghai Tannery Co. (Ltd.), under an agreement with Russia, entered into a contract for the manufacture of 100,000 pairs of boots a month for 10 months. At this time the output of the company ran from 20,000 to 30,000 pounds of leather a month, but arrangements were made to increase

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this output to about 100,000 pounds a month. Seventeen additional drums were installed and great quantities of hides especially suited for the contract requirements were purchased at prevailing high prices. The company also provided for its needs in tanning extracts, etc., for 10 months ahead. One mishap after another is said to have interfered with the arrangements made by the tannery. Shipments of supplies were not made as promised, but finally, notwithstanding all the difficulties, a total of 61,700 pairs of boots were shipped to Vladivostok. The whole shipment was refused. The resulting loss is said to have compelled the company to liquidate its affairs. The managers of the Shanghai Tannery Co. (Ltd.) stated that during the year preceding the work on the contract the company had been able to show a profit for the first time since its inception. The duty on sole and cow hides imported into China amounts to about $1.87 per 133⅓ pounds, and on calfskins, kid, patent, and colored leathers approximately $5.25 per 133⅓ pounds. The *ad valorem* duty on other kinds of leather is 5 per cent.

**Determination of the Permeability of Leather.** E. NIHOUL. *Collegium* (London), June 1916, pp. 147-50. Three methods are examined: 1st, that described by Gayley (this JOURNAL, Feb., 1916); 2nd, Thuau's method, *Collegium*, No. 414, p. 229; 3rd, the method of immersion. Kilp's apparatus, described by Gayley, subjects a sample clamped to the bottom of a tube to the pressure of a column of water, and provides an electrical contact which stops a clock when the moisture gets through. Nihoul remarks that the result will depend largely on the part of the hide from which the sample is taken, and the region sampled should therefore be stated. He suggests that instead of noting the time required for the first drop to penetrate, the quantity of water running through in a given time be measured. The Thuau method places the sample over the mouth of a Procter filter bell or an ordinary funnel, to which it is cemented with varnish or collodion. The funnel is connected to an exhaust pump, and a vacuum of 45 centimeters (about 18 inches) of mercury maintained while the leather is plunged in water. The time required for 10 cc of water to come through is noted. The third method is as follows: A piece of the leather 5 centimeters square is taken from the same part of the hide from which the sample to be analyzed is taken. It is weighed air dry, and then plunged into 30 or 40 cc. of water at 15° C. for ½ hour and then hung up for 10 minutes to drain and weighed. It is then reimmersed for 24 hours, again drained and weighed. The quantity absorbed in ½ hour should not exceed 35 per cent., or 50 per cent. in 24 hours for heavy leather, and for necks or flanks 40 per cent. for ½ hour and 55 per cent. in 24 hours.

Chrome leather should be tested by boiling a piece 10 centimeters (4 inches) square for 5 minutes. The edges should not curl, and it should not be hard when dried. The author tested samples of three types of sole leather in March last. Increases in weight after 12 hours for the three types were 11.4, 14.8 and 18.4 per cent. respectively, and after 24 hours,

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20, 21.4 and 26.8 per cent. Water-solubles in the same order were 34.9, 17.4 and 19 per cent., and hide substance 38.62, 48.38 and 40.53 per cent. None contained any free sulphuric acid nor mineral adulterants. Nihoul remarks that one might expect the heavily loaded leather to absorb water greedily and so gain in weight more than the less heavily loaded. It is notable, however, that the water in which the heavily loaded samples were soaked was much darker in color than the others. The small gains were therefore due to losses of soluble material.

EDITOR'S NOTE.—Professor Nihoul's suggestion that it might be better to measure the amount of water coming through in a given time, rather than the time for the dampness to get through, would lead to difficulties in testing American sole leathers tanned by the pit method. Such leathers are usually not wet through in two weeks! The time required for 10 cc. to flow through would be indefinitely great, for the water would evaporate as fast as it came through.

L. B.

**Second National Exposition of Chemical Industries.** The second exposition will be held at the Grand Central Palace, New York, week of September 25, 1916. The annual meeting of the American Chemical Society will be held the same week. The American Electrochemical Society will meet the latter part of the week. Beside the chemical exhibits, many moving pictures illustrating chemical manufacturers will be shown. Some of the films which will be shown are as follows: The making of black powder; manufacture of iron, of fertilizers and of varnish; mining and manufacture of iron; silver mining; asphalt; making of silk and of blotting paper. The exhibits will be on the second floor of the building, and most of the spaces are already taken. The auditorium is being enlarged for the accommodation of the societies which are to meet there, the seating capacity being increased to 500. There will be a "Southern Opportunities" section displaying the kinds of wealth which abound in the South in an undeveloped condition, for the information of chemists, engineers and capitalists. The Bureau of Mines is preparing an elaborate working exhibit. Dr. Charles H. Herty, President of the American Chemical Society and Chairman of the Exposition Advisory Committee, will make the opening address of the Exposition. Francis A. J. Fitzgerald, President of the American Electrochemical Society, and Arthur B. Daniels, President of the American Paper and Pulp Association, will also make addresses. The American Chemical Society, whose annual meeting will be in session at Columbia University, will hold conference meetings in the nature of symposia at the Exposition, which will be addressed by leaders in the field of industry under discussion. The Chemists Club, which is a few squares from the exposition building, has been selected as the headquarters of the American Chemical Society, and on Monday afternoon the Council of that Society will hold a business meeting there, followed by a dinner tendered to the Council by the New York Section.

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The Chemists Club offer the use of the lobby of the clubhouse for registration of members of the American Chemical Society.

The American Electrochemical Society has arranged a series of very interesting meetings beginning on Thursday morning, September 28, with the "Maid in America" technical session at the Grand Central Palace. This session will be devoted to papers and discussions on the great and varied electrochemical industries of America. This will be followed on Friday morning by another technical session, devoted to the theoretical side of electrochemistry. Registration will be held on Wednesday evening at the Exposition. Headquarters of the Electrochemical Society will be at the Electrochemical Society booth at the Exposition. The Technical Association of Pulp and Paper Industry who are also holding meetings in conjunction with the exposition, are arranging their headquarters in the midst of the "Paper and Pulp Industry" Section on the second floor of the Grand Central Palace. A large number of interesting papers are promised on the technical aspects of Pulp and Paper Manufacture. On Friday morning the meeting will be held in the auditorium at the Grand Central Palace, and the afternoon meeting will be a joint conference with the American Chemical Society. The members of the American Chemical Society and the American Electrochemical Society, who register with their societies, will receive badges which will admit them to the exposition without further tickets.

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Journal of the

# American Leather Chemists Association

Vol. XI OCTOBER, 1916 No. 10

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## COUNCIL MEETING.

The Council met at the Adelphia Hotel, Philadelphia, Sept. 1, 1916. The following members were present: H. C. Reed, T. A. Faust, F. H. Small, W. K. Alsop, C. R. Oberfell.

Committees were arranged for as follows:

Analysis of Tannery Wastes: W. A. Fox, Chairman, to appoint his own committee, to include F. W. Ames.

Dye Testing of Leather with Natural and Artificial Dyestuffs: Guy T. Creese, Chairman, Dr. William Klaber. Other members to be appointed by the Chairman.

Soaking of Hides, with Particular Reference to the Solubility of Hide in Salt Solutions and the Effect of Alkali on the Soaking of Dry Hides: Dr. L. Balderston, Chairman, to appoint his own committee, with the request that he include a member of the Graton and Knight Company's force.

Ash Determination in Tanning Materials and Leather: R. E. Porter, Chairman, to appoint his own committee.

The Secretary was instructed to ascertain where it is possible to obtain authentic type samples of moellons, and to report to the Council.

Disinfection of Hides: C. R. Oberfell, Chairman, to select his own committee. This committee is instructed to offer its services to the National Association of Tanners, to co-operate with them in any manner which they may designate.

Analysis of Sulphonated Oils: W. K. Alsop, Chairman, to select his own committee.

Extract Analysis: R. H. Wisdom, Chairman, to select his own committee.

Effect of Hard Water on Tannin: T. A. Faust, Chairman, to select his own committee.

Free Sulphuric Acid in Leather: C. R. Oberfell, Chairman, to select his own committee.

Mr. Oberfell emphasized the importance of collecting data on the tannin content of various tanning materials, so as to arrive at a reliable statement of the average tannin value of each. Several members participated in the discussion, but no action was taken.

The subject of members whose dues were unpaid was dis-

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cussed, and it was decided to stop the JOURNAL from those who did not pay up.

The President was authorized to solicit information in regard to the treatment of anthrax, and arrange such material for publication in the JOURNAL.

The matter of taking a poll of the Association in regard to a head for the Research Institute was discussed. It was decided not to do so unless the National Association of Tanners desire it.

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## ADDITIONS TO THE METHODS.

The Secretary announces the result of the voting on proposed provisional methods as follows:

Analysis of one-bath chrome liquors—yes, 49; no, 3.

Analysis of chrome leather—yes, 49; no, 3.

Analysis of lactic acid—yes, 49; no, 4.

The proposed paragraphs are therefore adopted as provisional methods. The text is printed in the March number, pages 89 to 91.

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## PRACTICAL SIGNIFICANCE OF THE SOLUBLE NON-TANNIN MATTERS OF VEGETABLE TANNING MATERIALS.[1]

*By Hugh Garner Bennett, M. Sc., F. C. S.*

All vegetable tanning materials when infused with water yield up to the solution not only tannin but also other substances, which exist normally in the tanning material and are soluble, but which are certainly not tannin, though some are closely related to the tannins. These substances are often spoken of as the "soluble non-tannins," which inclusive term is a kind of definition, albeit a rather vague one. According to this merely negative definition, every soluble substance is included, unless it be tannin. These are the substances it is proposed to discuss in the present article.

These non-tannins or (non-tans) are often mentioned as if they were a definite group of substances of similar nature and composition, like "tannins," "oils," "skins," etc. This is far from being the case. The term "non-tannin" includes substances

[1] S. & L. Rep. March 30, 1916.

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of a very widely differing nature, indeed it would be difficult to conceive of a collection of substances more different in essential character and composition and yet included under the same name. It is important to bear this in mind, for in discussions as to the value or harmfulness of non-tannins, this point has often been overlooked or ignored, and non-tans generally have reaped the credit for one particular ingredient, or the discredit due to another ingredient.

In considering the practical value of a tanning material, after allowing for the nature and amount of the tannin itself, it is not too much to say that the nature and amount of the various non-tannins are the most valuable criteria for pronouncing a verdict on any particular material. Hence it is a matter of considerable practical importance to have a clear idea as to what these non-tannins consist of, and also as to which of them are of real value in tanning, which of them are harmful, and which of them are simply superfluous. Very frequently one man recommends a tanning extract or a material because it contains "those valuable non-tannins," whilst another man recommends another extract because it is comparatively free from such substances. Very seldom is it known why such matters are valuable or harmful. It is proposed to make this clearer by dividing the soluble non-tannin matters into five typical groups of substances, according to their chemical nature and to discuss these groups in turn.

## I. The Sugars.

The first non-tannins to be considered are the "sugars," using the term in its broadest sense. The sugars are a well known class of substances which include some of our most valuable foods, *e. g.*, cane sugar (sucrose), milk sugar (lactose), fruit sugar (fructose) and grape sugar (glucose). Practically all tanning materials contain some sugar, but the quantity is exceedingly varied. Moreover they are not always present in the free state, *i. e.*, as a true non-tannin, but sometimes also are feebly combined with the tannins. The most important and most plentiful of these sugars is glucose, often present as a glucoside of the tannin, though not always so. Ordinarily glucose is thus a normal constituent of vegetable tanning materials, of vegetable tan liquors, and consequently also of vegetable-tanned leather.

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Nevertheless, the quantity is not large, and it is generally considered that not more than 2.0 per cent. of glucose which has been derived from the vegetable tanning materials can exist in leather. Thus if a chemist finds more than this in any sample of leather, he is justified in concluding that all the excess over 2.0 per cent. has been deliberately added. Indeed, in Britain, where glucose is seldom used for weighting purposes, a leather with over 2.0 per cent. glucose gives evidence of bad management in the tannery. This glucose has missed its valuable function to the tanner, *viz.*, to ferment and produce acids. This fermentation of sugars to acids is the normal destiny of the saccharoses, and herein lies their practical value as non-tannin matter. It is clear that if the tannage needs acid, *i. e.*, if "sour" liquors are wanted, the use of those tanning materials which yield sugars will be an advantage, and (other things being equal) that material which contains the most natural sugar is to be preferred. Thus of two extracts of equal tannin strength and similar nature, that in which the non-tans have a larger proportion of glucose or other sugars is the more valuable from a practical point of view. Conversely, of course, if a "sweet" tannage is required the sugary tanning materials are not wanted and the sugar fermentations should be prevented as far as possible.

In this connection it will be of interest to give a table showing the usual amount of sugar in the common tanning materials. The tanning materials have been purposely divided into the two familiar groups of "pyrogallol tans" and "catechol tans," and it is of considerable practical significance to note that, broadly speaking, it is the former which are sugary materials and yield sour liquors, whilst the latter show little sugar, and in consequence yield sweet liquors which often need artificial acidification. Pine bark (*Abies excelsa*) is, however, an exception to this rule, being a catechol tan with much associated sugar. Oak bark, the other apparent exception, probably contains a mixture of both pyrogallol and catechol tannins. The figures in the following table show the amounts of sugar calculated in each case to 100 parts tannin, which is the practical point of value.

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TABLE I.

*Pyrogallol Tannins.*

| Material | Sugar % of Tan |
|---|---|
| Myrobalans | 17.4 |
| Valonia | 9.5 |
| Divi-divi | 20.5 |
| Algarobilla | 19.1 |
| Sumac | 16.6 |

*Catechol Tannins.*

| | |
|---|---|
| Hemlock bark | 5.8 |
| Mimosa bark | 3.2 |
| Quebracho | 1.0 |
| Cube gambier | 3.9 |
| Pine bark | 33.5 |
| Oak bark | 25.2 |

The fermentations by which the sugars are converted into acids are due to the action of the micro-organisms of the tan liquors. There are many such fermentations taking place simultaneously, but they are well typified by the two most important of them, *viz.*, the acetic fermentation and the lactic fermentation.

As the name implies, this consists in the formation of acetic acid. In this process there are two well defined stages, each of which is carried out by its own special organisms. The first stage is the common and well known alcoholic fermentation, in which sugar is acted upon by various yeasts, yielding carbonic acid gas, which largely escapes into the air, and ordinary alcohol. This fermentation is often visible to the naked eye. If an infusion of myrobalans or valonia be made with warm water, and a liquor of about 40° Bk. be drawn off, in a very few hours this liquor, if kept in a warm place, will show obviously much the same fermentation as occurs in the manufacture of beer, exhibiting froth, bubbles of carbonic acid gas and the characteristic alcoholic and yeasty odor. The writer has found that the small quantity of sugar in mimosa bark is particularly susceptible to this fermentation. It is almost impossible to keep a mimosa bark liquor without this fermentation occurring in a very short time.

The second stage in the acetic acid fermentation is brought about by bacteria, *e. g., bacterium aceti,* which follows up the action of the yeasts, and converts the alcohol into acetic acid in

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a manner quite analogous to the formation of vinegar. The acetic acid formed in this way is a valuable adjunct in tanning and it is of some importance to notice that both these stages are necessary for its production. The writer has often observed the simultaneous formation also of acetic ester (ethylacetate), which is a compound derived from alcohol and acetic acid, but whether this be due to a totally different fermentation, or whether it be either an intermediate or a subsequent stage of the above fermentations, he has not as yet been able satisfactorily to determine. The occurrence of this ester in practice is rather in the leaches than in the tan liquors and is most obvious when the tannery material is about half "spent" or leached.

The lactic fermentation, which is the other chief fermentation of non-tannin sugars, consists in the formation of lactic acid from these sugars. This fermentation is brought about by many species of micro-organisms—several kinds of bacteria, both *micrococci* (round shaped bacteria) and *bacilli* (rod or dumb-bell shaped) produce this result. Non-tannin sugar is also fermented to lactic acid by a yeast (*S. acidi lactici*), and adding this yeast to the liquors may, under favorable circumstances, induce this fermentation. This lactic fermentation is not usually so extensive as the acetic fermentation, but is very valuable, for lactic acid is an exceedingly important and useful constituent of sour liquors and its "plumping" propensities are now well known. Occasionally the lactic acid so formed is itself fermented by another organism into butyric acid, but this fermentation is not usually extensive, nor is it to be encouraged.

It is obvious that if a tannery possess liquors which are too sweet, *i. e.*, short of these acids, these fermentations could be easily induced by adding glucose to the liquor. Usually this would be sufficient, but in some cases where these fermentations are practically absent it might be advisable to add also the ferments themselves, *e. g.*, the alcoholic and lactic yeasts. As most of the liquors of the modern tannery are too sweet, this point has practical importance, but in Britain tanners are usually too much afraid of getting glucose into their leather to adopt this course. Nevertheless such a course would be more natural and more economical than to buy expensive pure acids, like commercial

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acetic, lactic, formic and butyric acids, and add these to the liquors, as is now often done.

Another point in this connection is that ferments also exist which are capable of completely wasting non-tannin sugar, and indeed often do so. These organisms ferment sugars to materials which are not plumping acids and which have no practical value. The yeast *Mycoderma vini,* for example, fements sugars not to alcohol, but directly to carbon dioxide and water, and is a very common source of loss. The occurrence of this yeast is very noticeable as it grows profusely as a gray scum on the surface of tan liquors, soon multiplying so as to cover the whole surface and then forming a characteristic wrinkled cover, which often appears brown owing to the color of the tan liquor. This troublesome ferment is difficult to get rid of but it may be kept down by disturbing the liquor frequently. It is essential for this organism to have plenty of air, so that it may also be hindered to some extent from developing by pushing it down under the surface of the liquor, *i. e.,* in effect, by drowning it!

## II. Proteid Matters.

The proteids are highly complex organic matters which are an essential feature in all living cells and which constitute the bulk of all animals, and a large and very important part of all vegetable matters. They vary in many of their properties and are classified accordingly, but they have much the same ultimate composition and the same .general constitution. The following figures may be taken as representing approximately the lowest and highest limits in composition:

| Element | Percentage |
|---|---|
| Carbon | 49.0–55.0 |
| Hydrogen | 6.4– 7.3 |
| Nitrogen | 15.0–19.0 |
| Oxygen | 17.0–26.0 |
| Sulphur | 0.3– 5.0 |

The characteristic feature of these bodies is the high percentage of nitrogen. Selecting illustrations which are familiar to the leather manufacturer we may note 18.1 per cent. nitrogen in gelatin and 16.3 per cent. in hair. It will be clear that by estimating the amount of nitrogen in tanning materials, a fair idea of the amount of proteid matter can be obtained. This has been

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recently done by the writer (*Collegium*,[1] 1916, p. 1) and it will be of some interest in this connection to summarize the results.

TABLE II.

| Tanning Material | Percentage of Nitrogen | Milligrams of Nitrogen per Gram of Tannin |
|---|---|---|
| Myrobalans | 0.56 | 18.1 |
| Valonia cup | 0.29 | 10.4 |
| Valonia beard | 0.34 | 9.0 |
| Natal bark | 0.87 | 26.8 |
| Sicilian sumac | 0.87 | 35.2 |
| Lentisco | 1.18 | 69.2 |
| Quebracho wood | 0.17 | 8.4 |

These figures, of course, are variable, according to the different grades of material, just as the percentage of tannin varies in any material; but it will be noticed that very considerable differences obtain in the proportion of proteid matter and tanning matter. It should be remembered also that in leaching tannin it is not possible to obtain all these nitrogenous proteids in solution with the tannin. For example, the writer has shown that myrobalans extract contains about 45 per cent. of the total nitrogenous matters, and that quebracho extract contains about 27 per cent. of the total nitrogen of the wood. Some of these nitrogenous matters are insoluble in water, and some, though soluble in water, are insoluble in tannin solutions. Nevertheless, the soluble non-tannins of tanning materials contain some of these proteid matters and probably also some of their products of decomposition. Hence these nitrogenous non-tannins must be taken into consideration.

It must be asked then, "Have these nitrogenous matters any practical value?" The answer is undoubtedly "Yes." It is true that their valuable function is somewhat indirect, and largely unrecognized by tanners, but it is none the less real. They provide food for the organisms which bring about the acid fermentations of the sugars described above. These proteids are thus an essential condition for the production of the acid fermentations. Indeed the valuable work of Andreasch indicated that, providing sufficient sugars were available, the amount of acids produced is proportional to the amount of nitrogenous matters present in the liquors.

Now the practical point of importance is that it is not easy to

[1] This J., June, 1916, pp. 311-14.

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make tan liquors which contain sufficient of these proteids on account of their limited solubility, especially in tannin solutions, and also because their amount is never very great (as shown in Table II). Hence, the presence of a comparatively high proportion of proteids in a tanning material is of real value to the tanner, and it will be understood that even if the sugars are present in sufficiently large amounts there may be still failure to obtain sour liquors on account of the shortage of proteids. Where sweet liquors are required the significance of the proteids is equally obvious. Even a sugary material may be employed if the microbes are starved of nitrogen.

Undoubtedly some of the proteid matters of the tan liquors are derived from the hide itself, partly by chemical action and partly by the action of putrefactive bacteria which come forward with the hides from the soaks, limes, bates, puers, drenches, etc., and "acclimatize" themselves to the new conditions in the acid tan-liquors. But dissolving hides either by acids or by putrefaction is obviously an undesirable way of providing nitrogenous food for other microbes, for the conservation of hide substance is a matter of vital importance to the tanner. It is questionable how far the nitrogenous matter of tan liquors is derived from the hides and from the tanning materials, but it would seem clear that the strong fresh liquors containing nearly tanned goods would not support many putrefactive organisms, and that most of the nitrogen in these liquors is derived from the tanning materials. Indeed the fact that the acid fermentations occur as readily in the leaches as in the layer liquors indicates that this is the case. On the other hand the weak and nearly exhausted liquors containing untanned goods will provide a better field for the putrefactive organisms which provide nitrogenous food for the acid ferments. Now as the sugars are mostly fermented in the strong liquors and leaches it appears to the writer that the proteids in tanning materials have a practical importance which is greater than has been hitherto realized.

The most suitable "blends" of tanning materials have been largely determined empirically, *i. e.*, by actual practical experience as to results produced, rather than by inquiry into causes and calculated effects, but if any tanner will consider carefully his own blends in the light of Table I and Table II, he will begin

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to understand the significance of blending a material containing a high proportion of sugar (though it contain little proteid) with a material containing a high proportion of proteid, (though it contain little sugar). He will also understand the behavior of a material like quebracho, which contains little sugar and little proteid.

### III. The Phenolic Non-tannins.

This term has been selected by the writer to cover those substances which in chemical nature are somewhat similar to the tannins, and which are frequently related to them. These bodies are also derivatives of the phenols, and (except the flavone of fustic), they all contain either the catechol or the pyrogallol groups, and exhibit many of the reactions characteristic of these groups. There are many of these substances which are fairly well known, their actions and properties having been investigated. These phenolic non-tannins have in common the property of being absorbed by hides and by partly tanned leather, and this absorption profoundly modifies the nature of the tannage produced by the materials with which they are associated. Their practical importance is therefore very great and their influence far reaching. Much laborious work has been done to clear up their chemical nature and to form estimates of their practical value, but much more of such work yet remains to be done. It is with reference to this section of the soluble non-tannins that there are still differences of opinion as to their significance in the tannery. All tanning materials have some of these soluble non-tans associated with them so that it is impossible to get rid of their influence. It is highly probable, indeed, that many of the tests for distinguishing the various tanning materials can be explained by differences in the associated phenolic non-tans rather than by differences in the tannins themselves. It is important, however, to insist that although these bodies are near relatives of the tannins, they are actually not tannins, *i. e.*, they will neither make leather nor give a precipitate with a 1 per cent. gelatine, 10 per cent. salt solution.

For the purposes of this article the three chief types of phenolic non-tannins may be briefly discussed, flavones, catechins and acids.

Flavones are the coloring matters naturally associated with the

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tanning materials. They occur usually as soluble glucosides. Either acids or organized ferments break these up and liberate the coloring matters as yellow crystalline bodies sparingly soluble in water. They are soluble in alcohol and (like many tannins) are precipitated by lead acetate. Their coloring properties are most strongly developed by the use of metallic mordants. The chemical constitution of these bodies has been cleared up by the work of Perkin & Kostanecki, and their close relationship to the associated tannins is illustrated by the fact that both yield much the same decomposition products.

*Quercetin,* $C_{15}H_{10}O_7$ (1 : 3 : 3′ : 4′ tetra-hydroxy-flavonol) and its glucosides, are found associated with many catechol tannins such as quebracho, gambier, cutch, mimosa barks and oak barks, but especially in quercitron bark (*Quercus tinctoria*). Quercetin itself contains the catechol group. It is also found, however, associated with a few pyrogallol tans such as French sumac (*Coriaria myrtifolia*). It is the commonest coloring matter of the tanning materials. Its decomposition products are phloroglucol and protocatechuic acid.

*Myricetin,* $C_{15}H_{10}O_8$, 1 : 3 : 3′ : 4′ : 5′ pentahydroxy-flavonol) and its glucosides, are found associated with many tanning materials containing the pyrogallol group such as Sicilian sumac, myrobalans, and lentisco. This group is contained by the coloring matter itself also. Its decomposition products are phloroglucol and gallic acid.

Other flavones are found in tanning materials of less commercial importance such as *fesetin,* $C_{15}H_{10}O_6$, (3 : 3′ : 4′ trihydroxy-flavonol) which occurs in Venetian sumac, and *morin* $C_{15}H_{10}O_7$ (1 : 3 : 2′ : 4′ tetrahydroxy-flavonol), an isomer of quercetin which is the coloring matter of fustic (*Morus tinctoria*).

The practical significance of these non-tannins is that they very largely determine the color of the leather which is produced. Indeed, materials like fustic and quercitron-bark, which contain comparatively large quantities of these dyestuffs, are used for the express purpose of modifying the color of the leather. The flavones mostly dye yellow shades especially if alum or tin mordants are used. They are not the only coloring matters associated with the tannins, however, so that their influence in determining the color of the leather is not supreme. There is also the in-

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fluence of the phlobaphenes (or "reds") which are associated with the catechol tans. The phlobaphenes are difficultly soluble tannins, rather than non-tans, and are therefore, outside the scope of the present article. Nevertheless, it should be noted that the blend of phlobaphenes (reds) and flavones (yellows) is the predominant factor in producing the "tan" color of vegetable-tanned leather. Of course, if a tanning material contain neither flavone nor phlobaphene, an exceedingly light colored leather will be obtained. This is apparently the case with celavinia pods.

Another point worth noting is that these coloring matters largely determine the colors obtained in many qualitative precipitation tests for tanning materials, *e. g.*, the lime water test.

Catechins are soluble non-tannins which have such a close similarity in chemical behavior that they are distinguished from each other with great difficulty. They have all the same ultimate composition, expressed by the formula, $C_{15}H_{14}O_6$. They are white crystalline bodies, sparingly soluble in cold water, but freely soluble in hot water, alcohol, ether, ethyl acetate and in tannin solutions. They are precipitated by albumin, lead acetate and mercuric chloride, but (unlike the tannins) not by gelatin, alkaloids or tartar emetic. They give the phloroglucol reaction and are decomposed into phloroglucol and protocatechuic acid. With concentrated sulphuric acid they give deep purple colorations. Several individual members of this series have been isolated and investigated. The chief differences between them are that they combine with different amounts of water and melt at different temperatures. On boiling with dilute sulphuric acid they yield a series of phlobaphenes (or "reds"), and this has given rise to the theory that they are the parent substances of some of the tannins. They all contain the catechol group and are associated with practically all the catechol tans, but are especially prominent in gambier and cutch.

The practical value of these bodies is open to question. Speaking of the gambier catechin Procter says—"It probably possesses no tanning properties itself, but its anhydrides will tan. In experiments made by the writer a slight tanning effect was observed in a cold saturated solution, which had a faint yellow color and probably contained a trace of anhydrides, and on boiling the solution for some time the tanning effect was increased

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and both the liquid and the leather took a deeper and redder color. Its value is therefore uncertain, but the practical results from gambier seem larger than corresponds to the ready formed tannins present and it is not improbable that in the tanning process the catechin is gradually converted into available tannins."

The catechins are certainly absorbed by hide to some extent, but whether that is desirable or not is questionable. Some observers have thought that their absorption is not likely to interfere with the absorption of tannin, and is therefore bound to help in getting good weight. Others have thought that the catechins are first absorbed in the tanning process, and afterwards expelled by the tannins, that in a sense they prepare the way for the tan. In the opinion of the writer, the catechins are absorbed by hide permanently, and give weight, but they prevent in this way the absorption of a certain amount of tannin which would give more weight. On the whole therefore they prevent good weight rather than help to obtain it.

The catechins are not wholly disadvantageous, however, for they undoubtedly reduce the astringency of the natural tannins in liquors of the same apparent strength, and in this way they are valuable in the "green" or weak liquors of the tannery. They "mellow" the liquor and prevent drawn grain. In liquors which form a "sweet" tannage, the catechins (though possibly preventing good weights) assist materially in giving a soft mellow leather. In sour liquors, where a hard firm leather is required, their presence in the weak liquors of a tannery is still advantageous, for on account of their mild astringency they give the plumping acids their chance. In fact, the catechins may be said to plump the hides indirectly, *i. e.*. their substitution for astringent tannin allows a greater amount of plumping by other agents.

The phenolic acids are also closely allied to the tannins and are products of their decomposition. Gallic acid, $C_7H_6O_5$, is the best known of these bodies, as it is generally found associated with the widely employed pyrogallol tannins. It exists in the free state in many tanning materials notably in "babla," and is a product of the fermentation or decomposition of many of the tannins, such as sumac, myrobalans, oak galls, celavinia, etc. It is a crystalline body soluble in water, and more so in tannin solutions. It contains the pyrogallol group and gives many of the

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reactions of the pyrogallol tannins (see *Shoe and Leather Reporter,* 1911, March 16, p. 41[1] and also 1914, Sept. 17, pp. 33, 35 and 37[2]). It is precipitated by many reagents which also precipitate these tannins. It does not precipitate gelatine, however, and will not make leather. Unlike tannin, its solution gives no precipitate with tartar emetic and ammonium chloride, lead acetate in acetic acid, lead nitrate and several organic bases and basic coloring matters.

There is little doubt that its practical value is nil. In the average tannery it is absorbed by hide to some extent, as is shown by the analysis of the liquors by the Lowenthal method, but it probably prevents rather than assists the absorption of tannin (as in the case of catechin). Dr. Parker states positively that its presence is injurious, in that it dissolves leather, (*Collegium,* 1912, No. 498, p. 54[3]). As it is not usually present in great amounts in the fresh liquors, its presence in older liquors undoubtedly indicates the decomposition and waste of tannin. Molds are very liable to attack some of the pyrogallol tans and yield gallic acid. On the whole the verdict on gallic acid is unfavorable, but in justice to it, it should be noted, that as it is an acid it has a little value in the first tan liquors for the purpose of neutralizing lime. In a sweet tannage this is sometimes important. Where weight is not important and a soft leather is required, gallic acid will certainly assist its production.

The other phenolic acids have been little investigated as yet. Protocatechnic acid is the analogous decomposition product of the catechol tannins, but the writer is not aware that it has been actually found in the free state in such materials or in liquors made from them. It is a crystalline substance with a composition represented by its formula $C_7H_6O_4$ and has similar properties to gallic acid, but contains the catechol group instead of the pyrogallol group, and reacts accordingly.

Valonia, oakwood and French chestnut extracts certainly contain in their soluble non-tannins some phenolic acids, which from their tests with iodine, ferricyanide, etc., appear to be neither gallic nor protocatechnic acids. They may be isomers or homologues. Further investigation of these bodies is very desirable.

[1] Abst. this J. 1911, p. 254.
[2] This J. 1914, pp. 436-42.
[3] Abst. this J. 1912, pp. 192-204.

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All these phenolic non-tannins have in common another property which is exceedingly awkward for chemists. They are to some extent absorbed by hide powder in the course of analysis just as they are absorbed by hide in the yard. In a previous article in the *Shoe and Leather Reporter* (1914, March 19, pp. 45, 47, and 49[4]), the writer has pointed out these errors. It is exceedingly important to note that not only is the tannin over estimated in most tanning materials, but the substances which are thus estimated as tannin are such that they are the least to be desired of all non-tannins, whose leather forming value is in most cases even less than nothing, for they interfere with the absorption of tannin.

## IV. Ligneous Matters.

In most tanning materials, but especially in those extracts made from woods containing small amounts of tannin, *e. g.*, French chestnut and European oakwood extracts there are soluble non-tannins which are ligneous matters. These substances occur also in extracts such as those of quebracho wood, which are treated with a reagent that dissolves lignine, *viz.*, bisulphite of soda. These ligneous matters form another class of soluble non-tannin matters. They are widely different from tannin in most respects, including their chemical constitution and chemical behavior. For example they are not oxidized by acid permanganate to anything like the same extent as the tannin and phenolic non-tannins. They resemble tan, however, in that they have a certain affinity for hide and for hide powder. These ligneous matters are the essential ingredients of the so-called "tanning extracts" which are made from wood pulp. These extracts are sometimes sold as if they were perfectly analogous to quebracho, chestnut, etc., and are sometimes used as adulterants for these extracts.

The practical significance of these ligneous bodies has been made clear by the work of Parker and Blockey (*Collegium*, 1912, p. 44[5]). These workers obtained the ligneous non-tans from chestnut and oakwood extracts by removing the tannin and phenolic non-tans with gelatin and hide powder successively. Their experiments indicate that the presence of these substances is

[4] This J. 1912, pp. 191-204.

[5] Abstr. this J. 1911, pp. 608-11.

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injurious in tanning as they prevent the absorption of the true tannins, and tannages in which ligneous matters are present give comparatively poor weights. Other writers have shown that many of the tannins are much less soluble in water in the presence of these ligneous matters, and this is an important consideration where concentrated tan liquors are employed.

There seems little doubt, therefore, that the presence of these soluble non-tannins is wholly undesirable.

The ligneous extracts mentioned above, are, however, often used in commerce to load the leather after the ordinary tannage is completed. Whatever may be the ethics of this system, it certainly cannot make these ligneous non-tans into tanning matters (see *Shoe and Leather Reporter,* 1911, Oct. 19, p. 31[6]).

### V. Inorganic Salts.

Along with the soluble non-tannins discussed above, there are also the class of inorganic salts, which in themselves are not tanning agents, but have the property of influencing profoundly the effect of the other tanning matters. Some of these salts are naturally associated with the tanning materials especially in the case of the fruit tans, myrobalans, valonia, etc., and notably in palmetto extract. They are the normal but alkaline salts of weak organic acids. The writer has found that some of these acids are volatile.

The practical effect of these salts is to cause the mellowness of the tannage. This effect is explained by Procter as "probably due in the first place to the action of neutral salts in diminishing the energy of weak acids, and secondly to the fact that their bases combine to some extent with the tannins and that such tannins are, as it were, partially paralyzed in their action on hide. Sodium sulphite acts powerfully in this case." The writer has experimented on this point, in consultation with Prof. Procter, taking the mimosa bark tannin as a typical case of an astringent tannin, and he can very strongly confirm the above statement. The greater this effect is observed the softer the leather that results. Other salts which have been found to produce an effect in the same sense are alum, acetates of lime and soda, sulphate of magnesia and borax. Probably many other salts will act similarly. This softening effect is not overcome by the plumping

[6] Abstr., this J., 1911, pp. 608-11.

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acids. The mellowness of the natural tannery materials may sometimes be explained by this cause, although other causes produce similar effects.

Sharp astringent tannins, like quebracho are not only solubilized by sodium bisulphite but the nature of the tannin is profoundly modified by the usual bisulphite treatment. The tannin is much mellowed.

Where mellowness is needed and soft leathers are desired, this effect of inorganic salts is practically advantageous, but it may be the cause of much trouble and annoyance when other results are desired. There is always some little advantage, however, in the salts produced by the acids of the tan liquors (acetic, lactic, etc.) and the lime they have neutralized. These salts mellow the early tan liquors and assist materially in preventing drawn grain.

Common salt (sodium chloride) is found as a soluble non-tannin in some materials, notably in mangrove bark and extract. Its presence is undesirable as it tends to give thin flat leather.

These five classes of soluble non-tannins, *viz.*, sugars, proteids, phenolic non-tans, ligneous matters and salts are the chief ingredients in the ordinary non-tans. Other non-tans doubtless exist also in minor amounts such as starches, dextrins, etc., but the effects produced by the five classes discussed above go far to explain the differences in the practical effects of the different tanning materials.

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## WATTLE BARK AS A TANNING AGENT.[1]

*By A Cape Tanner.*

It seems worth while at the present time to call the attention of tanners in the United Kingdom to the value and relative cheapness of wattle barks for tanning purposes. So many factors decide the feasibility of adopting a new and special material, that to give more than a few hints is a difficult matter. The present seems an opportune time for giving a wider application to the use of these barks. They can be used both for the production of heavy leathers, requiring firmness, and lighter leathers, requiring suppleness and mellowness. Of wattle barks, there are two or three well-defined varieties—the black wattle, the eland's wattle, the green wattle, and the golden wattle. It is not here necessary to dwell on their growth and origin, for such must be common knowledge to any tanner of experience. For the present purpose of this article I shall endeavor to describe the results obtained, and the methods employed generally throughout the Cape Colony and South African leather industry. Until before the war, most of the wattle bark received in Europe was used on the Continent, and recourse must largely be made to the tanning literature of these countries for any elaborate and scientific information as to the practical value of same for tanning purposes. The tannin value of this group of barks averages about 32 per cent., whilst the price is moderate, so that, compared with many other materials, they form one of the cheapest tanning agents. The tannin contained belongs to the catechol class, and Paessler points out that these barks possess only 30 to 35 parts of non-tannin matter to every 100 parts of tannin. He also states that, apart from their richness in tannin, the low percentage of non-tannin liquors made from wattle bark are far less prone to fermentation than those from most tanning materials. The tannin is easily extracted, and not more than 3 per cent. need be left in the spent bark. The same authority classifies the principal tanning materials in the following descending order in this respect:—Quebracho wood, wattle bark, oakwood extract, oak bark, divi-divi, and so on. Detailed analyses of the various merits of these barks from many sources have often appeared, so that for this

[1] Leather World, Aug. 17, 1916.

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present purpose I will confine my remarks to a practical experience in their uses alone. In judging their efficiency and economy, these analyses, however, offer a good indication of their tanning merits, but both must be tested in practice. There is often a wide margin between the amount of tannin obtained by analysis and that available in producing leather. When properly used and understood, wattle barks prove one of the most important tannins of the catechol series; they spend easily, and give a high barkometer reading and tannin strength. They do not sour so much with the passage of goods, and are very astringent, and yield a leather of good color, of a slightly reddish tinge, but not nearly so red as oak or hemlock. Time being of such importance in the tannery of to-day, few waste a great deal of it in leaching material to make liquors—at least this applies to British tanners. In all cases, however, some leaching must be done, if only to take the materials which previously have been used for layers or dusting down.

The indifference to bark grinding is often responsible for many unsatisfactory results in leaching. Unless this is most carefully done, good extraction is practically impossible, no matter how it is carried out, hence it is from lack of attention in this direction that many tanners are surprised to see, upon analysis, their spent barks contain so much tannin, after having used so much hot water and heat. The chemist receives a sample of spent bark, and reduces it to a coarse meal in order to get every trace of soluble matter from it. There are few establishments, however, in which the average leaching will run below 3 per cent. An intelligent application in the methods of leaching therefore goes far to the subsequent successful working of the tanyard. It must be conducted in the manner best adapted for percolation and saturation of water or liquor through it, and not around it, and at the same time through the interstices of the mass of ground bark, through the pores and intercellular spaces of the bark itself. With South African tanners this is perhaps carried out more rigidly, since extracts, by reason of the extra freightage and cost of transport, makes their use more prohibitive, and therefore a subsidiary tannage.

As is very well known, there are many styles of bark-grinding machines in use, from the coffee mill type to the disintegrator.

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The former are very defective, principally on account of the irregular work performed. When the mill is set open, the bark is too coarse for saturation, and when set close, so fine as to prevent circulation in the leach, and not infrequently a mixture of both at the same time is the result. In most cases the arrangement of the knives does not permit of their clearing the chopped bark freely after making the cut, and therefore creates a mixture of shavings and dust, which does not leach well. The best method of grinding is with the disintegrator, which under favorable conditions performs good work. The ideal preparation of wattle bark is to cut it straight across the end in slices of not over one-eighth inch in thickness; these, with the rolling or mixing given in the conveyor, can be reduced to cubes very susceptible to saturation. A medium therefore should be arrived at between coarse and fine, and dull knives should never be permitted. When too fine it causes "clogging," and creates channels in the leaches, and never extracts with satisfaction. Of the two methods in common vogue for leaching, the press system is the most suitable for wattle bark, though it does not perhaps permit of such high-graded liquors—but these are usually supplemented at a later stage by the use of extract. On the other hand, the "open diffusion," or continuous pumping-over system, does permit of very high barkometer readings reaching as high as 130°. The press method allows the bark to be always covered with water, and shows liquors containing little soluble matter, and upon analysis the proper precentage of tannin for their gravity. In the "open diffusion" method, the water or liquor takes the most direct route to the suction pipe of the pump, and the upper bark does not get a due proportion of water, therefore it is imperfectly leached.

The best tanning results at the Cape are obtained by the press system. Next to the preparation of the bark, and relative to the leaching, is the question of temperature. Heat is absolutely necessary to remove the last portions of the available tannin in order that the bark may be swollen and thus disintegrated to an extent sufficient to admit of the removal of the soluble matter. It must not, however, be applied on the head or fresh leaches, as it would remove a quantity of matter that is insoluble in cold water or liquor, and becomes objectionable in the yard. In oper-

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ating leaches, it is very important that they be kept flooded continually; that is, covered as nearly as possible, in order that the bark may be kept in partial suspension and the circulation thus maintained, even throughout the entire mass. The opinion is very common that wattle barks in themselves are not entirely satisfactory as a tanning agent, and must be blended with other materials of the pyrogallol class, but it seems to me in practice a mistaken idea, due to the over-cautious temperament and conservative character of the British tanner, that its qualities are not more fully understood.

It is a bad practice to return spent handlers to the leaches again, as I have seen many tanners do. In most yards the barkometer is still the standard of testing the strength of a liquor, and it would require considerable ingenuity to devise a more deceptive method of determining its tannin value. A liquor of 15° B., which should contain 3.25 per cent. soluble matter, 68 per cent. of which is tannin and 32 per cent. non-tannin, will, when it reaches the tail row of a series of eight leaches, show approximately 9° B., but instead of containing 1.31 per cent. of tannin and 0.52 per cent. non-tannin, which a fresh 9° liquor should contain, it will only contain 0.69 per cent. tannin, the balance, 1.25 per cent., being non-tannin. As already stated, it is the return to the leach of this spent liquor, so rich in non-tannin, charged with acids, that causes much of the trouble in the yard liquors. The remedy for this evil is obvious: pump this sour filthy liquor down the sewer, but before doing so, be sure the liquor is spent.

I have found it a good practice in making up liquors to fill a leach with fresh ground bark, let it soak a few hours, and begin the strongest handler, then the next, and so on, until all the handlers are made up. It can then be filled up with clear water. The first handler should register not less than 3°, the second 4°, the third 6° and the last of six about 12° B. The first two handlers are either swung in on sticks, or suspended in mechanical rockers, and in some cases grained in a drum from the washing with a weak fresh liquor for a few minutes, and immediately transferred to the handler. These several methods are a matter of individual taste; personally, I favor the rockers. The above, of course, is for dressing leathers: for sole leathers

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the method would be different. Between this stage and the lay-away, some use floating liquors, made up with a little added myrobalans or extract; others between the handlers and laya-ways continue the process with drum tannage.

A very useful part of ground wattle bark is the dust, which frequently contains 60 per cent. of tannin. This is a valuable material for coloring sheep or goat and other light leathers when dissolved for paddle or drum tannage, and provides a splendid base for future stained or color requirements. The color of all finished wattle tannages should be light, and in the case of bag and harness leathers especially so.

To sum up, wattle bark possesses the following advantages:

(1) It is being produced in ever-increasing quantities, and presents no danger of a failure in supply.

(2) It is produced mainly in British territories.

(3) It seldom varies in quality.

(4) Its tanning value is rich.

(5) The tannin is easily extracted.

(6) Can be leached with great advantage in admixture with other materials.

From this comprehensive statement it should be clear to the unprejudiced and practical mind that wattle barks have come to stay. They are comparatively cheap, economical in use, and a useful material in the tanyard of to-day. Time and a fair trial may prove to even the sophisticated that they eclipse many other materials now commanding inflated prices.

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## ABSTRACTS.

**The Story of Chestnut Extract.** R. W. GRIFFITH, *S. and L. Rep.*, July 6, 1916. This paper is an interesting account of the plant and operations of the Champion Fiber Co., Canton, N. C., with two pages of half-tone illustrations.

**New Methods of Utilizing Babul Pods for Tanning.** *London Times Imperial and Foreign Trade Supplement*, July. Babul pods, obtained from the tree that also produces the gum arabic of commerce, have long been known to contain a notable quantity of tannin (18 to 20 per cent.). Owing to the fact that the tan liquor prepared from the pods rapidly undergoes fermentation and thus deteriorates before the hides or skins immersed in it have become completely tanned, the use of this material has not hitherto

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been adopted by tanners. As the result of laboratory experiments conducted by the Department of Industries at Cawnpore, it is claimed that this obstacle to the utilization of the product can be removed. It is found that by the addition of a very small quantity (0.3 to 0.5 per cent. of the weight of the pods) of crude carbolic acid to the infusion of the pods, fermentation is retarded to such an extent that the tan liquor can be used with satisfactory results. It has also been observed that the tendency of the tan liquor to ferment varies with its temperature. Below 60° F. babul pods may be used with a very small addition of antiseptic or with none at all. As an alternative to carbolic acid, phenazole slightly acidified with acetic acid may be used. The pods can be had in India for the cost of collecting them. From the Sudan, where they are known as garad (or sunt) pods, there is already a small export, which could be largely increased if a sufficient demand arose. The export value in the Sudan is about $34 per ton. The same product has also been occasionally exported from West Africa under the name of Gambia pods.

**Celpech Manufacture in Germany.** CONSUL GENERAL J. G. LAY. *Commerce Reports.* The German term "Zellpech" may be translated as "sulphite-cellulose pitch," and is the name given to the product made by evaporating down the sulphite lyes from the wood pulp process. The annual production of lye in Germany is about 700,000 tons. Fifty tons of dry "pitch" may be obtained from 654 cubic yards of lye. The lye is neutralized with milk of lime, filtered through coke and evaporated to about 33° Bé. It is then dried by an apparatus similar to that used for making powdered extract. The product is used as a binder in making coal briquettes and also in molding sand. It is also used in making cheap black dyes for rough cotton goods, and to impregnate sailcloth, fish nets, etc. It is also used in briquetting iron ore.

**Large Exports of Hides from China to United States.** *Commerce Reports.* In spite of unfavorable conditions in some quarters the export of hides from China during 1915 was greater than in preceding years and in some respects established a record. Germany, heretofore one of the heaviest buyers of hides from China, and Austria and Turkey, also good markets for some kinds of hides, were, of course, unable to take any at all. The United States became the purchaser of the stock that had formerly gone to some of these countries and took a great deal more besides. As a result it is estimated that from 50 to 75 per cent. of all the hides exported from China during this year went to the United States. The demand there may have been caused by the increased output of automobiles and war supplies, particularly shoes and leather garments. Prices, which were extremely low at the close of the preceding year, advanced rapidly about the middle of 1915 and increased as much as 75 to 100 per cent. in some instances by the end of the year, showing an average increase of 6 or 7 per cent. over the average price for the previous year. The total export of cow and buffalo hides for 1915 showed an increase of

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59,866 pounds, or one-tenth of 1 per cent., in spite of the fact that several of the best markets were closed throughout the year. The value of the export shows an even greater increase, $741,317, or about 7 per cent. Between one-third and one-half of all the cow hides exported from China in 1915 went to America, the only two other countries taking any considerable amount being Italy and Japan. Germany and Austria were formerly good markets for this export. Prices advanced about 40 per cent. over the 1914 figures. There was practically no export of buffalo hides because of the closing of the German and Turkish markets, which formerly consumed about 90 per cent. of the output. Experiments in tanning these hides in America were unsuccessful, which is one reason why none were purchased there. As a result, it is said, the Chinese have practically ceased killing their buffaloes, and there are now more of these animals living in China then ever before. Of the 8,000,000 goatskins exported in 1915, from 75 to 90 per cent. were sent to the United States. Probably a much larger number would have been exported had it not been for disturbances in several of the Provinces from which many goatskins come. A great many are now said to be held up awaiting an opportunity to ship them safely. The prices at the close of the season were about 50 per cent. higher than the closing rates of the previous year. About three-fifths of the 250,000 untanned sheepskins exported went to the United States. This number is considerably smaller than the export for 1914, owing principally to the fact that large contracts were made by the allies for sheepskins tanned with the wool on and made into rugs and clothing for use at the front. This is also true with respect to raw furs of all kinds, for which there was a large demand from England and Russia at almost any figure for military purposes tanned and made into rugs or clothing. Prices in consequence have advanced as much as 100 per cent. in some instances.

**Hides and Skins from Bahia.** *Commerce Reports.* Hides and Skins are important articles of export from this city, having been sent from here to all countries in the past three years in the following quantities:

| Items | 1913 | 1914 | 1915 |
|---|---|---|---|
| Dry hides (number) | 258,000 | 225,000 | 463,052 |
| Green hides (number) | 101,500 | 99,000 | 104,459 |
| Goatskins (bales of about 250 skins each) | 3,532 | 2,217 | 5,039 |
| Sheepskins (bales of about 220 skins each) | 1,396 | 1,151 | 1,489 |

These large exports were due to a combination of high prices and the necessary slaughter of many animals, because of the lack of pasture (due to drought) on which to maintain them. It is now (June 10) said, however, that with the copious rains in the early months of 1916, pasture is again plentiful, and that far fewer hides and skins are now being received here for shipment than at the corresponding time last year. The average f. o. b. price of prime dry hides and seconds, taken together, was around 25 cents per pound at the beginning of 1915 and around 27 cents at the close of the year. At first the seconds formed about 30 per cent. of the whole number shipped, but owing to the drought, and the consequent large

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number of "fallen" hides, the proportion rose to at least 50 per cent. at the end of the year. Green, or wet salted, hides averaged from about 14.5 to 15.5 cents per pound f. o. b. vessel throughout the year, and dry salted hides from 21 to 23.5 cents. Goats and sheep are much less likely to die from the effects of drought in this country than cattle, although when the animals suffer from hunger their skins become thin and papery in texture and decrease in value. The probable output of skins here will probably not be so much reduced as that of hides during 1916. Goatskins varied little in price in 1915, averaging about 20 cents per pound f. o. b. throughout the year. Sheepskins, which are sold by the skin and not by weight, averaged about 45 cents per skin f. o. b.

**Concessions Asked for Quebracho Plant in Paraguay.** CONSUL SAMUEL HAMILTON WILEY. *Commerce Reports.* A representative of American capitalists petitioned the Paraguayan Congress on July 6, 1916, to grant a concession for the erection and operation of a plant for the manufacture of extract of quebracho in Paraguay. The most important concession asked is a readjustment of the export duties on extract of quebracho. It is asked that the present fixed rate of export duty on extract of quebracho, 10 gold pesos ($9.65) per ton (2,240 pounds), be abolished and an export duty of 1 gold peso ($0.965) per ton be established on extract of quebracho when the market value of this commodity does not exceed 100 gold pesos ($96.50) per ton. The quotations of extract of quebracho on the bourse of Buenos Aires shall determine the market price for the purposes of levying export duty. When the market price of extract of quebracho exceeds 100 gold pesos per ton an *ad valorem* duty of 4 per cent. shall be paid on the value exceeding the 100 pesos per ton, in addition to the 1 peso per ton to be paid on the first 100 pesos market value. In addition to this, concessionaire asks for exemption from import duties of machinery and other materials to be used in the construction and operation of the plant and exemption from fiscal imposts. In consideration for the granting of the concession, the concessionaire agrees to advance the sum of 500,000 gold pesos ($482,500) as a loan to the Paraguayan Government. This loan is to bear interest at the rate of 5 per cent. per annum and the amortization thereof shall be effected from the export duties that shall be due the Paraguayan Government for quebracho extract exported by the plant. The loan is to be made on the date of the signing of the concession and the amortization of the debt is to begin on the day set in the concession for the plant to commence operation—January 1, 1918. The concessionaire also binds himself to produce not less than 15,000 tons of quebracho extract per annum.

**Anthrax in Bristles.** Editorial *Leather World*, Sept. 7, 1916. A shipment of shaving brushes made in Japan from Chinese or Manchurian materials was found to be infected with anthrax. They had been widely distributed before suspicion was directed against them. A consignment was traced to Newcastle, and on examination these were found to contain anthrax spores.

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**Rhodesia May Develop Leather Industry.** *British and South African Export Gazette*, through *Commerce Reports*. It is thought by many that the manufacture of leather, if seriously undertaken in Rhodesia, might be carried on profitably, and in time render the territory independent to a large extent of the imported article. In various localities the farmers tan the hides themselves, but only in a desultory way. However, some of them assert that by their own rough processes they have been able to obtain a leather even more durable than that derived from Europe or America. Wattle bark, it is stated, is not used in these processes, the bark of two native trees being employed in place of it. One of these is believed to contain at least as great a percentage of tannin as wattle. A large amount of money would not be needed to give leather manufacture a fair trial. The outlay would comprise the cost of a small water-tight tank, and the simplest of whatever machinery is used for the purpose of finishing the tanned hide, with a few inconsiderable sundries. When the British Trade Commissioner visited Rhodesia recently he was so impressed with the specimens he saw that he discussed the possibility of manufacturing leather and leather goods on a commercial scale. Commenting on the abnormally high price now commanded by leather in Rhodesia, an officer of a development company says: "We still dispose of our many hundreds of hides for export to speculators, securing the lowest possible return, and pay for the manufactured article an enormous price, covering as it does the cost of shipment and rail, several middlemen's, and the retailer's profits."

## PATENTS.

**Machine for Sponging Leather. U. S. Patent 1,193,927.** CARLETON RUHR, Olean, N. Y.

**Tanning. U. S. Patent 1,191,480.** OTTO SCHMIDT, assignor to the Badische Company. Skins are tanned by treatment with a product made from naphthalene, sulphuric acid and formaldehyde. This product is amorphous, soluble in water, free from dyeing properties and capable of precipitating glue or gelatin.

**Process for Unhairing Hides. U. S. Patent 1,197,519.** GUSTAV MAAG, New York. The hides are subjected to the action of a solution of sodium sulphide at a temperature of 95° F. the strength of the solution being 1.5° Bé and the quantity of sodium sulphide 10% of the weight of the hides.

**Machine for Brushing Leather. U. S. Patent 1,195,859.** CARLETON RUHE, Olean, N. Y.

**Mechanical Tanning Machine. U. S. Patent 1,195,858.** CARLETON RUHE, Olean, N. Y. The tanning liquid is circulated by means of pumps.

**Flaying Device. U. S. Patent 1,192,451.** W. PFEFFERKORN, Zug, Switzerland.

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**Machine for Stretching Hides. U. S. Patent 1,193,042.** DANIEL MERCIER, Annonay, France.

**Artificial Leather. U. S. Patent 1,192,460.** C. ROESSLER, Hamburg, Germany. The composition consists of 100 parts leather waste, 20 parts asbestos, 162 parts magnesia, 10 parts kieselguhr, and 15 parts of coloring matter, ground together and mixed with 75 parts of Epsom salts.

**Flushing Machine. U. S. Patent 1,192,728.** A. BAJOHR, Brooklyn, N. Y.

**Elastic Leather. U. S. Patent 1,192,691.** M. SCHEUER, New York, N. Y. A coating of elastic material is applied to leather while the leather is stretched, and it is dried while stretched.

**Machine for Cleaning Skins. British Patent 5467.** J. H. BROGDON, Hexham, England.

**Tanning of Hides and Skins. U. S. Patent 1,191,527.** E. W. MERRY, Sheffield, England, assignor to International Pyrotan Co., Ltd., London. The materials used are alum and sodium pyrophosphate, from 5 to 7 parts of alum crystals to 1 part anhydrous sodium pyrophosphate. The quantity of alum is about 10 per cent. of the weight of hide, and the quantity of water from 20 to 40 per cent. of the weight of hide.

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## CORRECTIONS.

In the October issue, p. 531, second and twelfth lines from bottom for "protocatechnic," read "protocatechuic." Page 532, footnotes; that numbered 4 should be numbered 5, and footnote 4 should read "Abstr., this J., 1914, p. 243."

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## METHODS OF THE A. L. C. A.

### OFFICIAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR THE ANALYSIS OF VEGETABLE MATERIALS CONTAINING TANNIN.

#### I. Raw and Spent Materials.

(1) CAUTION:

Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations. (See "General" under Sampling.)

(2) PREPARATION OF SAMPLE:

The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(a) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(b) Samples of raw material too wet to be ground may be dried before grinding as in (a). In this case a preliminary water determination must be made according to (IV) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) WATER DETERMINATION:

Ten grams of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

(4) AMOUNT OF SAMPLE TO BE EXTRACTED:

Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 gram tannin to 100 cc. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) EXTRACTION:

Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. The container shall be provided above

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with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) Woods, Barks and Spent Materials:

Five hundred cc. of the percolate shall be collected outside in approximately 2 hours and the extraction continued with 500 cc. for 14 hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give condensation approximately 500 cc. in 1½ hours.

(B) Materials Other than Woods, Bark and Spent:

Digest the material in the extractor for 1 hour with water at room temperature and then extract by collecting 2 liters of percolate outside in approximately 7 hours.

(6) ANALYSIS:

The percolate shall be heated at 80° C., be cooled, made to the mark and analyzed according to the official method of extracts.

## II. Analysis of Extract.

(7) AMOUNT AND DILUTION FOR ANALYSIS:

(A) Fluid Extracts:

Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gram tannin to 100 cc. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during

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weighing. Dissolve the extract by washing it into a liter flask with 900 cc. of distilled water at 85° C.

Cooling:

(a) The solutions prepared as above shall be cooled rapidly to 20° C. with water at a temperature of not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with at once, or

(b) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below 20° C., be brought to 20° C. with water at not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with.

(B) Solid and Powdered Extracts:

Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred cc. of distilled water at 85° C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred until a homogeneous solution is obtained. When dissolved, the solution shall immediately be washed into a liter flask with 800 cc. of distilled water at 85° C., be cooled, etc., as under (a) above.

NOTE: It is permissible to make up 2-liter instead of 1-liter solutions dissolving by washing into flask with 1,800 cc. water at 85° C. in case of fluid extracts and 1,700 cc. water at 85° C. in case of solid or powdered extracts.

(8) TOTAL SOLIDS:

Thoroughly mix the solutions; pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying." (See IV.)

(9) WATER:

The water content is shown by the difference between 100 per cent. and the total solids.

(10) SOLUBLE SOLIDS:

S. & S. No. 590, or Munktell's No. 1 F, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 grams kaolin

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digested with 200 cc. of distilled water at 20° C. for 1 hour shall not give more than 1 mg. of soluble solids per 100 cc., and shall be neutral to phenolphthalein. To 1 gram kaolin in a beaker add sufficient solution to fill the paper, stir and pour on paper. Return filtrate to paper when approximately 25 cc. has collected, repeating operation for 1 hour, being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying so soon as it becomes CLEAR. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 cc. of clear filtrate into tared dish; evaporate and dry as under (8).

(11) INSOLUBLES:

The insoluble content is shown by the difference between the total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) NON-TANNINS:

The hide powder used for the non-tannin determination shall be of woolly texture well delimed and shall require between 12 and 13 cc. of N/10 NaOH to neutralize 10 grams of the absolutely dry powder.

(a) Digest the hide powder with 10 times its weight of distilled water till thoroughly soaked. Add 3 per cent. of chrome alum, $(Cr_2SO_4)_3K_2SO_424H_2O$, in 3 per cent. solution calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with 4 successive portions of distilled water, each portion equal in amount to 15 times the weight of the air-dry powder taken. Each digestion shall last for 15 minutes, and the hide powder shall be squeezed to approximately 75 per cent. water after each digestion except the last, a press being used if neces-

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sary. The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent. of water, not less than 71 per cent. nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approximately 20 grams. (See IV.) To such quantity of the wet hide as represents as closely as practicable 12½ grams (not less than 12.2 nor more than 12.8) of absolutely dry hide add 200 cc. of the original analysis solution and shake immediately for 10 minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 grams of kaolin (answering test described under (9) ) to the detannized solution and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 cc. of filtrate into tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnels and receiving vessels must be kept covered during filtration. Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

(b) Digest the hide powder with the amount of water and add the amount of chrome alum in solution directed under (a). Agitate in some form of mechanical shaker for 1 hour and proceed immediately with washing and subsequent operations as directed under (a).

NOTE: In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

(13) TANNIN:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

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### III. Analysis of Liquors.

(14) DILUTION:

Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature it is permissible to dilute with water at 80° C. and cool rapidly as described under (7, A, a).

(15) TOTAL SOLIDS:

To be determined as in Extract Analysis.

(16) SOLUBLE SOLIDS:

To be determined as in Extract Analysis.

(17) INSOLUBLES:

Determined as in Extract Analysis.

(18) NON-TANNINS:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73 per cent. water, corresponding to an amount of dry hide powder shown in the following table:

| Tannin range per 100 cc. | Dry powder per 100 cc. |
|---|---|
| 0.35——0.45 gram | 9.0——11.0 grams |
| 0.25——0.35 gram | 6.5—— 9.0 grams |
| 0.15——0.25 gram | 4.0—— 6.5 grams |
| 0.00——0.15 gram | 0.0—— 4.0 grams |

Solutions to be shaken for non-tannins as in Extract Analysis and 100 cc. evaporated as in Extract Analysis.

### IV. Temperature, Evaporation and Drying, Dishes.

(19) TEMPERATURE:

The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids and non-tannins must be identical at the time of pipetting.

(20) EVAPORATION:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer" at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

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(21) DISHES:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor more than 3 inches in diameter.

### V. Determination of Total Acidity of Liquors.

(22) REAGENTS:

(a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter is recommended to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of ½ gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

DIRECTIONS:

To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution, dilute with 50 cc. of water and titrate with tenth normal soda using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

### VI. General.

(23) When materials containing sulphite-cellulose extract are analyzed, the fact that the material contains sulphite-cellulose extract shall be noted on the report.

(24) The test for the presence of sulphite cellulose in a liquor or extract shall be as follows: Five cc. of a solution of analytical strength shall be placed in a test tube, 0.5 cc. of aniline added and the whole well shaken; then 2 cc. of strong hydrochloric acid added and the mixture again shaken. If at least as much precipitate remains[1] as is obtained when a comparison solution prepared as below is similarly treated, the material shall be held to contain sulphite cellulose.

[1] Neradol D gives the same reaction.

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The comparison solution shall consist of sulphite cellulose in the proportion of one part total solids to 2,000 cc. of solution, and as much tanning material, similar to that being tested, but known to be free from sulphite-cellulose, as will make up the solution to analytical strength.

(25) On public analytical work by members of this Association the fact that the Official Method has been used, shall be so stated.

### OFFICIAL METHOD FOR SAMPLING TANNING MATERIALS.

GENERAL:

Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of liquor which have been kept with no preservative in them for some time do not represent the condition of the liquor when sampled.

All extracts and crude tanning materials shall be sampled as nearly as possible at time of weighing, and for every 50,000 pounds, or less, sampled a sample shall be drawn.

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(1) SOLID, POWDERED AND PASTY EXTRACTS:

The number of packages to be sampled out of a given lot shall be ascertained by taking a percentage of the total number of packages in the lot obtained in the following manner:—Divide the total number of packages by 100, multiply by 0.02 and subtract from 4.

Thus $4{,}700 \div 100 = 47$

$47 \times 0.02 = 0.94$

$4 - 0.94 = 3.06$ per cent.

$4{,}700 \times 0.0306 = 144$ packages.

Provided that for lots of 200 packages and under 5 per cent. of the number of packages shall be sampled, and for lots of 10,000 packages and over 2 per cent. of the number of packages shall be sampled.

Whenever possible every Nth package shall be set aside for sampling while the extract is being moved. When this is not possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry, closed container. When sampling is completed, the whole composite sample shall be broken up until it will pass through a sieve of 1-inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of at least 6 ounces shall be drawn from opposite quarters by means of a small flat scoop (and not by selecting a handful here and there). The sample shall be enclosed in the smallest clean, dry, glass receptacle, sealed and properly labeled.

NOTE:—Whenever possible the sample should be wrapped in paraffine paper and placed in the smallest straight-side glass receptacle, especially is this desirable during the warmer months of the year.

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least 2 pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

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(2) LIQUID EXTRACTS IN BARRELS:

The number of barrels of extracts to be sampled out of any given lot shall be not less than 10 per cent. of the whole number of barrels for every 50,000 pounds or fraction thereof. The barrels to be sampled shall be rolled and shaken from end to end until the contents are homogeneous. Whenever this is not possible the heads of the barrels shall be removed and the contents stirred until homogeneous, a sample of equal size to be taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples of at least 4 ounces shall be drawn and preserved in clean, dry, glass containers; sealed and labeled with such distinguishing marks as may be necessary.

(3) LIQUID EXTRACT IN BULK:

The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) LIQUID EXTRACT IN TANK CARS:

The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE:—As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded:—A quart sample shall be taken from the discharge three minutes after the extract has begun to run; another quart sample shall be taken three minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be trans-

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ferred to a suitable container as soon as taken, be thoroughly mixed and sampled as in (2).

(5) CRUDE TANNING MATERIALS:

A. Shipments in bags, mats or other similar packages.

A number of packages shall be sampled representing 2 per cent. of the weight for every shipment of 50,000 pounds or fraction thereof, by taking representative portions from each package. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than 5 pounds each shall be preserved in air-tight containers properly labeled.

B. Shipments in bulk, bark, wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least 2 pounds in size be preserved in air-tight containers, as in "A."

(6) SPENT MATERIALS FROM LEACHES:

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least 1 quart in size be preserved for analysis.

(7) TANNING LIQUORS:

The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least 1 pint be taken for analysis. The addition of 0.03 per cent. of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered contain-

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ers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than 1 pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

### OFFICIAL METHOD FOR ANALYSIS OF VEGETABLE TANNED LEATHER.

(1) PREPARATION OF SAMPLE:

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) MOISTURE:

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) FATS:

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent may be used for the determination of water-soluble material.

(4) ASH:

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) WATER-SOLUBLE MATERIAL:

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for 3 hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

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(6) GLUCOSE:

SOLUTIONS.

*Copper Sulphate.*—Dissolve 34.639 grams of $CuSO_4.5H_2O$ in distilled water and dilute to 500 cc. Filter through asbestos.

*Alkaline Tartrate Solution.*—Dissolve 173 grams of Rochelle salt and 50 grams NaOH in water and dilute to 500 cc. Allow to stand 2 days and filter through asbestos.

*Normal Lead Acetate Solution.*—Prepare a saturated solution of normal lead acetate.

DETERMINATION.

Place 200 cc. of leather extract of analytical strength in a ½-liter flask, add 25 cc. of a saturated solution of normal lead acetate, shake frequently (5-10 minutes), and filter. (The funnels and beakers must be kept covered to prevent evaporation.) Add to the filtrate an excess of solid potassium oxalate. Mix frequently for 15 minutes and filter, returning the filtrate until clear. Pipette 150 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for 2 hours. Cool, neutralize (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 cc. of the copper solution and 25 cc. of the alkaline tartrate solution in a 400 cc. beaker. Add 50 cc. of the clarified and neutralized solution above mentioned and heat to boiling in *exactly 4 minutes* and boil for 2 minutes.[1] Filter immediately without diluting, *through asbestos*,[2] wash thoroughly with hot water, then with alcohol, and finally with ether; dry for ½ hour in water oven and weigh as cuprous oxide, determine the amount of dextrose by the use of Munson and Walker's table (Bull. 107: Rev. Bu. of Chem., p. 243) and report in percentage on leather.

[1] The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 cc. copper soln. + 25 cc. alk. tartrate soln. + 50 cc. $H_2O$ in a 400 cc. beaker to 100° C. in exactly four minutes.

[2] The finely divided, long-fibered asbestos to be used in the glucose determination should be digested with $HNO_3$, washed, then digested with NaOH and washed. When Gooch filters are prepared, they should be washed with boiling Fehling's solution, then with $HNO_3$. The mats thus prepared can be used for a long time.

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## MUNSON AND WALKER'S TABLE

(Bulletin 107, Revised, Bureau of Chemistry, page 243.)
(Expressed in milligrams.)

| Copper (Cu) | Dextrose (*d*-glucose) | Copper (Cu) | Dextrose (*d*-glucose) | Copper (Cu) | Dextrose (*d*-glucose) |
|---|---|---|---|---|---|
| 8.9 | 4.0 | 44.4 | 21.3 | 79.9 | 38.9 |
| 9.8 | 4.5 | 45.3 | 21.7 | 80.8 | 39.3 |
| 10.7 | 4.9 | 46.2 | 22.2 | 81.7 | 39.8 |
| 11.5 | 5.3 | 47.1 | 22.6 | 82.6 | 40.2 |
| 12.4 | 5.7 | 48.0 | 23.0 | 83.5 | 40.6 |
| 13.3 | 6.2 | 48.9 | 23.5 | 84.4 | 41.1 |
| 14.2 | 6.6 | 49.7 | 23.9 | 85.3 | 41.5 |
| 15.1 | 7.0 | 50.6 | 24.3 | 86.2 | 42.0 |
| 16.0 | 7.5 | 51.5 | 24.8 | 87.1 | 42.4 |
| 16.9 | 7.9 | 52.4 | 25.2 | 87.9 | 42.9 |
| 17.8 | 8.3 | 53.3 | 25.6 | 88.8 | 43.3 |
| 18.7 | 8.7 | 54.2 | 26.1 | 89.7 | 43.8 |
| 19.5 | 9.2 | 55.1 | 26.5 | 90.6 | 44.2 |
| 20.4 | 9.6 | 56.0 | 27.0 | 91.5 | 44.7 |
| 21.3 | 10.0 | 56.8 | 27.4 | 92.4 | 45.1 |
| 22.2 | 10.5 | 57.7 | 27.8 | 93.3 | 45.5 |
| 23.1 | 10.9 | 58.6 | 28.3 | 94.2 | 46.0 |
| 24.0 | 11.3 | 59.5 | 28.7 | 95.0 | 46.4 |
| 24.9 | 11.8 | 60.4 | 29.2 | 95.9 | 46.9 |
| 25.8 | 12.2 | 61.3 | 29.6 | 96.8 | 47.3 |
| 26.6 | 12.6 | 62.2 | 30.0 | 97.7 | 47.8 |
| 27.5 | 13.1 | 63.1 | 30.5 | 98.6 | 48.2 |
| 28.4 | 13.5 | 64.0 | 30.9 | 99.5 | 48.7 |
| 29.3 | 13.9 | 64.8 | 31.4 | 100.4 | 49.1 |
| 30.2 | 14.3 | 65.7 | 31.8 | 101.3 | 49.6 |
| 31.1 | 14.8 | 66.6 | 32.2 | 102.2 | 50.0 |
| 32.0 | 15.2 | 67.5 | 32.7 | 103.0 | 50.5 |
| 32.9 | 15.6 | 68.4 | 33.1 | 103.9 | 50.9 |
| 33.8 | 16.1 | 69.3 | 33.6 | 104.8 | 51.4 |
| 34.6 | 16.5 | 70.2 | 34.0 | 105.7 | 51.8 |
| 35.5 | 16.9 | 71.1 | 34.4 | 106.6 | 52.3 |
| 36.4 | 17.4 | 71.9 | 34.9 | 107.5 | 52.7 |
| 37.3 | 17.8 | 72.8 | 35.3 | 108.4 | 53.2 |
| 38.2 | 18.2 | 73.7 | 35.8 | 109.3 | 53.6 |
| 39.1 | 18.7 | 74.6 | 36.2 | 110.1 | 54.1 |
| 40.0 | 19.1 | 75.5 | 36.7 | 111.0 | 54.5 |
| 40.9 | 19.6 | 76.4 | 37.1 | 111.9 | 55.0 |
| 41.7 | 20.0 | 77.3 | 37.5 | 112.8 | 55.4 |
| 42.6 | 20.4 | 78.2 | 38.0 | 113.7 | 55.9 |
| 43.5 | 20.9 | 79.1 | 38.4 | 114.6 | 56.3 |

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| Copper (Cu) | Dextrose (*d*-glucose) | Copper (Cu) | Dextrose (*d*-glucose) | Copper (Cu) | Dextrose (*d*-glucose) |
|---|---|---|---|---|---|
| 115.5 | 56.8 | 155.5 | 77.4 | 195.4 | 98.4 |
| 116.4 | 57.2 | 156.3 | 77.8 | 196.3 | 98.9 |
| 117.3 | 57.7 | 157.2 | 78.3 | 197.2 | 99.4 |
| 118.1 | 58.1 | 158.1 | 78.8 | 198.1 | 99.9 |
| 119.0 | 58.6 | 159.0 | 79.2 | 199.0 | 100.3 |
| 119.9 | 59.0 | 159.9 | 79.7 | 199.9 | 100.8 |
| 120.8 | 59.5 | 160.8 | 80.1 | 200.7 | 101.3 |
| 121.7 | 60.0 | 161.7 | 80.6 | 201.6 | 101.8 |
| 122.6 | 60.4 | 162.6 | 81.1 | 202.5 | 102.2 |
| 123.5 | 60.9 | 163.4 | 81.5 | 203.4 | 102.7 |
| 124.4 | 61.3 | 164.3 | 82.0 | 204.3 | 103.2 |
| 125.2 | 61.8 | 165.2 | 82.5 | 205.2 | 103.7 |
| 126.1 | 62.2 | 166.1 | 82.9 | 206.1 | 104.1 |
| 127.0 | 62.7 | 167.0 | 83.4 | 207.0 | 104.6 |
| 127.9 | 63.1 | 167.9 | 83.9 | 207.9 | 105.1 |
| 128.8 | 63.6 | 168.8 | 84.3 | 208.7 | 105.6 |
| 129.7 | 64.0 | 169.7 | 84.8 | 209.6 | 106.0 |
| 130.6 | 64.5 | 170.5 | 85.3 | 210.5 | 106.5 |
| 131.5 | 65.0 | 171.4 | 85.7 | 211.4 | 107.0 |
| 132.4 | 65.4 | 172.3 | 86.2 | 212.3 | 107.5 |
| 133.2 | 65.9 | 173.2 | 86.7 | 213.2 | 108.0 |
| 134.1 | 66.3 | 174.1 | 87.1 | 214.1 | 108.4 |
| 135.0 | 66.8 | 175.0 | 87.6 | 215.0 | 108.9 |
| 135.9 | 67.2 | 175.9 | 88.1 | 215.8 | 109.4 |
| 136.8 | 67.7 | 176.8 | 88.5 | 216.7 | 109.9 |
| 137.7 | 68.2 | 177.7 | 89.0 | 217.6 | 110.4 |
| 138.6 | 68.6 | 178.5 | 89.5 | 218.5 | 110.8 |
| 139.5 | 69.1 | 179.4 | 89.9 | 219.4 | 111.3 |
| 140.3 | 69.5 | 180.3 | 90.4 | 220.3 | 111.8 |
| 141.2 | 70.0 | 181.2 | 90.9 | 221.2 | 112.3 |
| 142.1 | 70.4 | 182.1 | 91.4 | 222.1 | 112.8 |
| 143.0 | 70.9 | 183.0 | 91.8 | 223.0 | 113.2 |
| 143.9 | 71.4 | 183.9 | 92.3 | 223.8 | 113.7 |
| 144.8 | 71.8 | 184.8 | 92.8 | 224.7 | 114.2 |
| 145.7 | 72.3 | 185.6 | 93.2 | 225.6 | 114.7 |
| 146.6 | 72.8 | 186.5 | 93.7 | 226.5 | 115.2 |
| 147.5 | 73.2 | 187.4 | 94.2 | 227.4 | 115.7 |
| 148.3 | 73.7 | 188.3 | 94.6 | 228.3 | 116.1 |
| 149.2 | 74.1 | 189.2 | 95.1 | 229.2 | 116.6 |
| 150.1 | 74.6 | 190.1 | 95.6 | 230.1 | 117.1 |
| 151.0 | 75.1 | 191.0 | 96.1 | 231.0 | 117.6 |
| 151.9 | 75.5 | 191.9 | 96.5 | 231.8 | 118.1 |
| 152.8 | 76.0 | 192.8 | 97.0 | 232.7 | 118.6 |
| 153.7 | 76.4 | 193.6 | 97.5 | 233.6 | 119.0 |
| 154.6 | 76.9 | 194.5 | 98.0 | 234.5 | 119.5 |

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| Copper (Cu) | Dextrose (*d*-glucose) | Copper (Cu) | Dextrose (*d*-glucose) | Copper (Cu) | Dextrose (*d*-glucose) |
|---|---|---|---|---|---|
| 235.4 | 120.0 | 275.4 | 142.2 | 315.3 | 164.9 |
| 236.3 | 120.5 | 276.3 | 142.7 | 316.2 | 165.4 |
| 237.2 | 121.0 | 277.1 | 143.2 | 317.1 | 166.0 |
| 238.1 | 121.5 | 278.0 | 143.7 | 318.0 | 166.5 |
| 238.9 | 122.0 | 278.9 | 144.2 | 318.9 | 167.0 |
| 239.8 | 122.5 | 279.8 | 144.7 | 319.8 | 167.5 |
| 240.7 | 122.9 | 280.7 | 145.2 | 320.7 | 168.0 |
| 241.6 | 123.4 | 281.6 | 145.7 | 321.6 | 168.5 |
| 242.5 | 123.9 | 282.5 | 146.2 | 322.4 | 169.0 |
| 243.4 | 124.4 | 283.4 | 146.7 | 323.3 | 169.6 |
| 244.3 | 124.9 | 284.2 | 147.2 | 324.2 | 170.1 |
| 245.2 | 125.4 | 285.1 | 147.7 | 325.1 | 170.6 |
| 246.1 | 125.9 | 286.0 | 148.2 | 326.0 | 171.1 |
| 246.9 | 126.4 | 286.9 | 148.7 | 326.9 | 171.6 |
| 247.8 | 126.9 | 287.8 | 149.2 | 327.8 | 172.1 |
| 248.7 | 127.3 | 288.7 | 149.7 | 328.7 | 172.7 |
| 249.6 | 127.8 | 289.6 | 150.2 | 329.5 | 173.2 |
| 250.5 | 128.3 | 290.5 | 150.7 | 330.4 | 173.7 |
| 251.4 | 128.8 | 291.4 | 151.2 | 331.3 | 174.2 |
| 252.3 | 129.3 | 292.2 | 151.7 | 332.2 | 174.7 |
| 253.2 | 129.8 | 293.1 | 152.2 | 333.1 | 175.3 |
| 254.0 | 130.3 | 294.0 | 152.7 | 334.0 | 175.8 |
| 254.9 | 130.8 | 294.9 | 153.2 | 334.9 | 176.3 |
| 255.8 | 131.3 | 295.8 | 153.7 | 335.8 | 176.8 |
| 256.7 | 131.8 | 296.7 | 154.2 | 336.7 | 177.3 |
| 257.6 | 132.3 | 297.6 | 154.7 | 337.5 | 177.9 |
| 258.5 | 132.7 | 298.5 | 155.2 | 338.4 | 178.4 |
| 259.4 | 133.2 | 299.3 | 155.8 | 339.3 | 178.9 |
| 260.3 | 133.7 | 300.2 | 156.3 | 340.2 | 179.4 |
| 261.2 | 134.2 | 301.1 | 156.8 | 341.1 | 180.0 |
| 262.0 | 134.7 | 302.0 | 157.3 | 342.0 | 180.5 |
| 262.9 | 135.2 | 302.9 | 157.8 | 342.9 | 181.0 |
| 263.8 | 135.7 | 303.8 | 158.3 | 343.8 | 181 5 |
| 264.7 | 136.2 | 304.7 | 158.8 | 344.6 | 182.0 |
| 265.6 | 136.7 | 305.6 | 159.3 | 345.5 | 182.6 |
| 266.5 | 137.2 | 306.5 | 159.8 | 346.4 | 183.1 |
| 267.4 | 137.7 | 307.3 | 160.3 | 347.3 | 183.6 |
| 268.3 | 138.2 | 308.2 | 160.8 | 348.2 | 184.1 |
| 269.1 | 138.7 | 309.1 | 161.4 | 349.1 | 184.7 |
| 270.0 | 139.2 | 310.0 | 161.9 | 350.0 | 185.2 |
| 270.9 | 139.7 | 310.9 | 162.4 | 350.9 | 185.7 |
| 271.8 | 140.2 | 311.8 | 162.9 | 351.8 | 186.2 |
| 272.7 | 140.7 | 312.7 | 163.4 | 352.6 | 186.8 |
| 273.6 | 141.2 | 313.6 | 163.9 | 353.5 | 187.3 |
| 274.5 | 141.7 | 314.4 | 164.4 | 354.4 | 187.8 |

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| Copper (Cu) | Dextrose (*d*-glucose) | Copper (Cu) | Dextrose (*d*-glucose) | Copper (Cu) | Dextrose (*d*-glucose) |
|---|---|---|---|---|---|
| 355.3 | 188.4 | 382.0 | 204.4 | 408.6 | 220.7 |
| 356.2 | 188.9 | 382.8 | 204.9 | 409.5 | 221.3 |
| 357.1 | 189.4 | 383.7 | 205.5 | 410.4 | 221.8 |
| 358.0 | 189.9 | 384.6 | 206.0 | 411.3 | 222.4 |
| 358.9 | 190.5 | 385.5 | 206.5 | 412.2 | 222.9 |
| 359.7 | 191.0 | 386.4 | 207.1 | 413.0 | 223.5 |
| 360.6 | 191.5 | 387.3 | 207.6 | 413.9 | 224.0 |
| 361.5 | 192.1 | 388.2 | 208.2 | 414.8 | 224.6 |
| 362.4 | 192.6 | 389.1 | 208.7 | 415.7 | 225.1 |
| 363.3 | 193.1 | 390.0 | 209.2 | 416.6 | 225.7 |
| 364.2 | 193.7 | 390.8 | 209.8 | 417.5 | 226.2 |
| 365.1 | 194.2 | 391.7 | 210.3 | 418.4 | 226.8 |
| 366.0 | 194.7 | 392.6 | 210.9 | 419.3 | 227.4 |
| 366.9 | 195.2 | 393.5 | 211.4 | 420.2 | 227.9 |
| 367.7 | 195.8 | 394.4 | 212.0 | 421.0 | 228.5 |
| 368.6 | 196.3 | 395.3 | 212.5 | 421.9 | 229.0 |
| 369.5 | 196.8 | 396.2 | 213.1 | 422.8 | 229.6 |
| 370.4 | 197.4 | 397.1 | 213.6 | 423.7 | 230.1 |
| 371.3 | 197.9 | 397.9 | 214.1 | 424.6 | 230.7 |
| 372.2 | 198.4 | 398.8 | 214.7 | 425.5 | 231.3 |
| 373.1 | 199.0 | 399.7 | 215.2 | 426.4 | 231.8 |
| 374.0 | 199.5 | 400.6 | 215.8 | 427.3 | 232.4 |
| 374.8 | 200.1 | 401.5 | 216.3 | 428.1 | 232.9 |
| 375.7 | 200.6 | 402.4 | 216.9 | 429.0 | 233.5 |
| 376.6 | 201.1 | 403.3 | 217.4 | 429.9 | 234.1 |
| 377.5 | 201.7 | 404.2 | 218.0 | 430.8 | 234.6 |
| 378.4 | 202.2 | 405.1 | 218.5 | 431.7 | 235.2 |
| 379.3 | 202.8 | 405.9 | 219.1 | 432.6 | 235.7 |
| 380.2 | 203.3 | 406.8 | 219.6 | 433.5 | 236.3 |
| 381.1 | 203.8 | 407.7 | 220.2 | 434.4 | 236.9 |
| | | | | 435.3 | 237.4 |

(7) NITROGEN:

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1907).

## REAGENTS.

*Standard Acid Solutions.*—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

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*Standard Alkali Solution.*—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

*Sulphuric Acid.*—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

*Sodium Hydroxide Solution.*—A saturated solution of sodium hydroxide free from nitrates.

*Potassium Sulphate.*—This reagent should be pulverized before using.

*Indicator.*—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

## DETERMINATION.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid from 5 to 15 minutes or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distill until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1½ hours. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

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## PROVISIONAL METHOD FOR THE ANALYSIS OF ONE-BATH CHROME LIQUORS.

*Chrome Determination.*—Dilute a measured quantity of the liquor with water to a definite volume so that the dilution contains from 0.15 to 0.25 per cent. of $Cr_2O_3$. To 10 cc. of this dilution in a 300 cc. Erlenmeyer flask add about 50 cc. of water and about 2 grams of sodium peroxide. Boil gently 30 minutes, adding water if necessary to keep the volume from falling below about 15 cc. Cool, neutralize with strong HCl and add 5 cc. excess. Cool again. Add 10 cc. of a 10 per cent. solution of potassium iodide. After 1 minute run in from a burette 0.1 N sodium thiosulphate until the iodine color has nearly disappeared; then add a few cc. of starch solution (1 gram per liter) and titrate to the disappearance of the blue. One cc. of 0.1 N thiosulphate is equivalent to 0.002533 gram $Cr_2O_3$.

*Acid Determination.*—Place 50 cc. of the above dilution in a 7-inch porcelain dish, add about 400 cc. of water and 1 cc. of a 5 per cent. solution of phenolphthalein and bring to a boil. While boiling, titrate with 0.5 N NaOH until the pink color persists after 1 minute boiling. One cc. 0.5 N NaOH is equivalent to 0.02002 gram $SO_3$, 0.02452 gram $H_2SO_4$, 0.01773 gram Cl or 0.01823 gram HCl.

*Basicity.*—The basicity is the ratio of basic radical to acid radical, found by dividing the percentage of $Cr_2O_3$ by the percentage of $SO_3$ or of Cl, carrying the quotient to two decimal places.

## PROVISIONAL METHOD FOR THE ANALYSIS OF CHROME LEATHER.

*Chrome Determination.*—(a) Ash 3 grams of leather. Mix the ash well with 4 grams of a mixture of equal parts of sodium carbonate, potassium carbonate and powdered borax glass and fuse for 30 minutes. Dissolve the cooled fusion in hot water with enough HCl to make the solution acid. Filter. If there is any residue on the filter, ash it and treat the ash with 1 gram of the fusion mixture in the same manner as the original ash, adding the solution to the first. Make up to 500 cc. To 100 cc. of this solution in an Erlenmeyer flask, add 5 cc. HCl and determine $Cr_2O_3$ as above in the analysis of one-bath chrome liquors.

(b) If it is not desired to determine Fe or Al, the ash of 3

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grams of leather may be transferred to an iron crucible, mixed with 3 grams of sodium peroxide and fused 10 minutes. Place cooled crucible in 300 cc. water in a casserole and boil 20 minutes. Wash into a 500 cc. flask, cool and make up to the mark. Filter through a dry filter. Place 100 cc. of filtrate in Erlenmeyer, neutralize with HCl, add 5 cc. excess and proceed as in (a).

**PROVISIONAL METHOD FOR SULPHONATED OILS.**

MOISTURE.

Weigh between 30 and 40 grams (depending on amount of water present) into a flask of 250 to 300 cc. and add 75 cc. water saturated xylol, prepared by heating a mixture of water and xylol with frequent shaking and subsequently removing the water in a separatory funnel. Connect to a Liebig condenser and place flask in a bath of paraffine or a heavy lubricating oil. Distil moderately until the distillate comes clear. Collect distillate in a tube graduated to 1/10 cc. and wash condenser with a stream of xylol from a wash bottle. Place graduated tube in hot water and when the distillate is clear, cool. The percentage of moisture is obtained by dividing the volume of water in the distillate by the weight of oil taken.

NOTE:—For the graduated tube Eimer & Amend's No. 3812 is recommended.

ASH.

Weigh any convenient quantity into a dish or crucible. Ignite gently, allowing the oil to burn and complete incineration until all carbon is consumed.

NON-SAPONIFIABLE.

Weigh approximately 10 grams of oil into an 8-ounce Erlenmeyer flask and add 5 cc. aqueous KOH solution (50 grams KOH in water and dilute to 100 cc.), 45 cc. ethyl alcohol and a few glass beads. Boil 1 hour with reflux condenser. Add 100 cc. water and cool. Transfer to separatory funnel and shake at least three times with petrolic ether (B. P. 40° to 75° C.) using 50 cc. each time. Wash ether layer at least three times with 50 cc. water containing 10 cc. ethyl alcohol. Use alcohol to break

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emulsion. Evaporate ether extract in tared vessel, cool and weigh.

NOTE:—If the contents of the flask bump violently during saponification add 25 cc. petrolic ether, and proceed.

### COMBINED $SO_3$.

(a) Weigh approximately 4 grams into an Erlenmeyer flask and boil for 40 minutes with 30 cc. HCl (1:5). Shake frequently. Cool, transfer to separatory funnel and shake out with petrolic ether. Draw off aqueous layer and wash ethereal layer with water. Combine washings with main aqueous portion and the sulphuric acid determine as barium sulphate. From the amount thus found, the quantity as determined in (b) is subtracted and the difference calculated as $SO_3$.

(b) Dissolve 4 grams in ether and shake out several times with 25 cc. concentrated brine free from sulphates. Combine the washings, dilute, filter and determine the sulphuric acid as barium sulphate.

### TOTAL FATTY OIL.

The total fatty oil shall be the difference between 100 per cent. and the sum of moisture, ash and non-saponifiable.

NOTE:—The results obtained by these methods shall be reported only in one decimal place.

**PROVISIONAL METHOD FOR ANALYSIS OF MOELLONS.**

### MOISTURE.

Weigh accurately 3 grams of the sample in a wide platinum dish, and heat with a low flame until the moisture is all driven off. This point can be determined by the appearance of smoke, and a slight crackling sound. Place the dish in a desiccator, cool and weigh.

### ASH.

Ash the moellon remaining in the dish after the moisture determination in the usual manner, cool and weigh.

### UNSAPONIFIABLE.

Weigh accurately in a 300 cc. flask, 5 grams of the moellon, add 2.5 grams caustic potash dissolved in a little water (or 5 cc.

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of a 50 per cent. KOH solution), and 25 cc. of 95 per cent. alcohol, boil with reflux condenser for 1 hour, shaking occasionally. Glass beads may be used to prevent bumping. Add 50 cc. hot water, cool, transfer to a separatory funnel, and extract three times, using 40 cc. petroleum ether for each extraction. A little alcohol may be added to break persistent emulsions. Wash the combined ether solutions three times with a mixture of 30 cc. of water and 10 cc. of alcohol, transfer to a tared dish, evaporate to dryness, cool and weigh. Excessive drying must be avoided.

### OXIDIZED FATTY ACIDS.

Boil the soap solution remaining from the unsaponifiable determination until all the alcohol is expelled, then dissolve in hot water, transfer to a separatory funnel, rinse the beaker thoroughly into the funnel, bringing volume to approximately 300 cc., and immediately add a slight excess of concentrated HCl (about 25 per cent. more than sufficient to neutralize total alkali). Rotate the contents of the flask vigorously, cool and shake out with petroleum ether. Run off the aqueous layer, and pour off the ether layer, avoiding any loss of oxidized fatty acids. Wash these acids twice with small quantities of petroleum ether and hot water; dissolve in warm 95 per cent. alcohol, filter if necessary, transfer to a tared dish, and place in an ordinary evaporator and dryer for 16 hours; then cool and weigh. The entire operation should be conducted without delay.

### FREE FATTY ACIDS.

Weigh out 1 gram moellon, dissolve in mixture of 20 cc. alcohol and 20 cc. sulphuric ether, which has been neutralized to phenolphthalein, and titrate with N/10 NaOH, using phenolphthalein as indicator. Test for mineral acids or alkalies (by adding methyl orange to the water emulsion of the moellon), and if present, make the necessary correction.

## PROVISIONAL METHOD FOR ANALYSIS OF HARD GREASES.

### TITER TEST.

Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Baumé) and 75 cc. of 95 per cent. by volume alcohol or 120 cc. of water. Boil to dryness with

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constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water and if alcohol has been used boil for 40 minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Baumé) to free fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry 20 minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 x 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 x 6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for 30 seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

### UNSAPONIFIABLE.

Same as for Unsaponifiable in Moellons.

### FREE FATTY ACIDS.

Same as for Free Fatty Acids in Moellons.

### PROVISIONAL METHOD FOR THE ANALYSIS OF LACTIC ACID.

*Free Sulphuric Acid.*—Dissolve 50 grams of the sample in 200 cc. alcohol, which should be neutral, and of at least 95 per cent.

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strength. Heat to 60° C., cover and let stand over night in a warm place. Filter off precipitated material and wash with alcohol. Evaporate off the alcohol, make up residue to 250 cc. with water, add 5 cc. strong HCl, boil, add $BaCl_2$ and determine $BaSO_4$ in the usual way. Calculate to per cent. $H_2SO_4$ on the original sample.

*Volatile Acid.*—Weigh out 1 gram of sample, make up to about 50 cc. with water, titrate with 0.5 N NaOH. Calculate

TABLE SHOWING THE RELATION OF AMOUNTS OF VOLATILE ACID FOUND IN DISTILLATE OBTAINED UNDER STANDARD CONDITIONS TO THE AMOUNTS ACTUALLY PRESENT IN DISTILLING FLASK, IN MILLIGRAMS.

One Distillation.

| In distillate | In flask | In distillate | In flask | In distillate | In flask | In distillate | In flask |
|---|---|---|---|---|---|---|---|
| 1 | 0.0 | 14 | 17.5 | 27 | 37.5 | 40 | 57.9 |
| 2 | 0.0 | 15 | 19.0 | 28 | 39.0 | 41 | 59.6 |
| 3 | 0.0 | 16 | 20.5 | 29 | 40.6 | 42 | 61.3 |
| 4 | 2.0 | 17 | 22.1 | 30 | 42.1 | 43 | 62.9 |
| 5 | 3.5 | 18 | 23.6 | 31 | 43.7 | 44 | 64.6 |
| 6 | 5.1 | 19 | 25.2 | 32 | 45.2 | 45 | 66.3 |
| 7 | 6.7 | 20 | 26.7 | 33 | 46.8 | 46 | 68.0 |
| 8 | 8.2 | 21 | 28.2 | 34 | 48.3 | 47 | 69.8 |
| 9 | 9.8 | 22 | 29.8 | 35 | 49.9 | 48 | 71.5 |
| 10 | 11.3 | 23 | 31.3 | 36 | 51.5 | 49 | 73.3 |
| 11 | 12.8 | 24 | 32.9 | 37 | 53.1 | 50 | 75.0 |
| 12 | 14.4 | 25 | 34.4 | 38 | 54.7 | 51 | 76.8 |
| 13 | 15.9 | 26 | 35.9 | 39 | 56.3 | 52 | 78.5 |

Two Distillations.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 5 | 0.0 | 22 | 19.2 | 39 | 38.9 | 56 | 58.6 |
| 6 | 1.0 | 23 | 20.4 | 40 | 40.0 | 57 | 59.8 |
| 7 | 2.0 | 24 | 21.5 | 41 | 41.1 | 58 | 61.1 |
| 8 | 3.0 | 25 | 22.7 | 42 | 42.3 | 59 | 62.3 |
| 9 | 4.0 | 26 | 23.9 | 43 | 43.4 | 60 | 63.5 |
| 10 | 5.0 | 27 | 25.0 | 44 | 44.6 | 61 | 64.7 |
| 11 | 6.2 | 28 | 26.2 | 45 | 45.7 | 62 | 65.9 |
| 12 | 7.4 | 29 | 27.3 | 46 | 46.8 | 63 | 67.2 |
| 13 | 8.6 | 30 | 28.5 | 47 | 48.0 | 64 | 68.4 |
| 14 | 9.8 | 31 | 29.7 | 48 | 49.2 | 65 | 69.6 |
| 15 | 11.0 | 32 | 30.8 | 49 | 50.3 | 66 | 70.8 |
| 16 | 12.1 | 33 | 32.0 | 50 | 51.5 | 67 | 72.0 |
| 17 | 13.4 | 34 | 33.1 | 51 | 52.7 | 68 | 73.3 |
| 18 | 14.5 | 35 | 34.3 | 52 | 53.9 | 69 | 74.5 |
| 19 | 15.7 | 36 | 35.4 | 53 | 55.0 | 70 | 75.7 |
| 20 | 16.9 | 37 | 36.6 | 54 | 56.2 | 71 | 76.9 |
| 21 | 18.1 | 38 | 37.7 | 55 | 57.4 | 72 | 78.1 |

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the result to lactic acid: (1 cc. 0.5 N NaOH = 0.045 gram lactic acid.) On this basis, make up a solution containing about 15 grams of acid per liter. Place 150 cc. of this dilution in a long-necked 300 cc. Kjeldahl flask, connected through a Kjeldahl bulb trap to a vertical spiral condenser, the total height from the bottom of the flask to the top of the turn connecting with the condenser being between 20 and 24 inches. Distill over 125 cc. in from 47 to 53 minutes, counting from the time the first drop falls into the receiver, which should be a graduated cylinder. Add 125 cc. of water to the residue in the flask and repeat. Titrate both distillates with 0.1 N NaOH and phenolphthalein and calculate result to grams of acetic acid: 1 cc. 0.1 N NaOH = 0.006 gram acetic acid. From these figures for acid found in distillates find actual weight of volatile acid placed in boiling flask, by means of table, and calculate this result to percentage of volatile acid in the sample.

*Free Acid and Anhydride.*—Titrate 50 cc. of the dilution made up for volatile acid, in the cold, with 0.5 N NaOH and phenolphthalein to first full pink. Call this figure "first titration." From it subtract a number of cc. of 0.5 N NaOH equivalent to the sum of volatile acid and free sulphuric acid present in the 50 cc. of dilution. (If the sample contains free oxalic or hydrochloric acid, the amount must be determined by appropriate methods, and further deduction made.) Calculate the remainder to lactic acid and express it as a percentage of the sample. This is the free lactic acid. After completing the first titration, add 4 cc. excess alkali, or in the case of concentrated acids 5 cc., and stand aside at room temperature (20°-25° C.), for 15 minutes. Then add 5 cc. 0.5 N $H_2SO_4$, boil, and titrate back with 0.5 N NaOH. The amount of alkali used by anhydride is now found by subtraction and calculated to lactic acid. Express this as per cent. of lactic acid equivalent to anhydride present in sample.

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## THE ESTIMATION OF CHROMIC OXIDE IN CHROME TANNED LEATHER.*

*By M. C. Lamb, F. C. S., and A. Harvey.*

It has been recently suggested that a standard should be set up of a percentage chromic oxide content for military chrome leather, and that this standard should be the minimum quantity of chromic oxide which will be allowed in the chrome upper leather of army boots. The percentage amount of chromic oxide present in a well tanned chrome leather is in the neighborhood of 3.0 per cent. The majority of chrome tanners employing the two bath (Schultz) method use about 5 to 6 per cent. of bichromate on the pelt weight; this the authors calculate to be equivalent to about 3.5 per cent. chromic oxide on the dry leather, allowing for varying differences in the moisture in the drained pelt prepared for tanning and the incomplete absorption of the whole of the contents of the bichromate and acid bath.

The considerable increase in the cost of all chrome salts has led several manufacturers to attempt economies by the substitution of a portion of the chrome salt necessary to make leather by a preliminary tannage with basic alum or basic alumina sulphate, followed by a correspondingly diminished amount of the chrome salt ordinarily used before the rise in price of bichromates. As to whether such a combination in the production of a leather which possesses the wearing qualities of a pure chrome leather, or not, the writers do not at the present juncture intend to discuss.

Without using alum or alumina sulphate either as a preliminary tanning agent, or in conjunction with chrome salts, it is a well known fact, that unless the leather gives 2.8 per cent. to 3.0 per cent. chromic oxide it will invariably be under-tanned. Many samples of chromic leather possessing tinniness and lacking the supple feel of well tanned leather, have invariably been found to yield a chromic oxide content below the minimum given above.

The considerable increase in price, and the short supply of nigrosine and other suitable black coal-tar dyestuffs used in dyeing chrome leather, has necessitated the partial, if not entire substitution of these products by the use of iron salts, thus reverting back to the older and less satisfactory method of dyeing blacks on chrome leather in use some ten years prior to the war.

* *Collegium*, London Edition, May, 1916, pp. 201-3.

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In carrying out the estimation of $Cr_2O_3$ in leather, as stated in the "Leather Chemists' Pocket Book," p. 193, the authors have, on several occasions obtained rather higher results than those expected. On investigating this point it was found to be due to the fact that the samples contained a proportion of iron.

Now, if this iron is not by some method eliminated before the estimation of the chromium it will eventually form $Fe_2Cl_6$. This will liberate iodine from KI, and so tend to give the high results referred to above. A slight alteration in the method has been adopted, which is stated below. At the same time the $Na_2CO_3$ fusion has been replaced by that with $Na_2O_2$ using a porcelain crucible.

The ash left from incinerating 5 grams of the leather is transferred to a porcelain crucible, where it is mixed with approximately 2 to 3 grams of sodium peroxide, and the whole gently heated. After the mass has been in a state of fusion for 10 minutes, it is cooled down and dissolved in water. The iron which now remains undissolved in the form of $Fe_2O_3$ is filtered off, and the filtrate treated as for the estimation of $Cr_2O_3$ in the usual way. When the removal of the iron has not been effected by filtration, the authors have obtained as much as 0.10 per cent. $Cr_2O_3$ over the correct amount, thus giving (on 0.5 per cent. $Cr_2O_3$), an error of more than 20 per cent. on the whole.

The use of large quantities of oil and fatty matters employed upon army chrome upper leathers, amounting in many cases to more than 10 per cent. calculated on the weight, renders it imperative that the percentage chromic oxide should be calculated on the weight of leather obtained after extracting the grease with a suitable solvent, and not merely calculating the chromic oxide on the weight of leather before removal of the fatty matter, an error which has been made by more than one of our colleagues, the misleading effect of which is shown in the parallel case below:

| | On original leather. Per cent. | Recalculated on degreased leather. Per cent. |
|---|---|---|
| Total ash and mineral matter | 3.00 | 3.35 |
| Chromic oxide | 2.57 | 2.87 |
| Oil and fatty matter | 10.60 | — |

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# COMPARATIVE SOLE-LEATHER TESTS WITH AUSTRALIAN PINE BARKS, AND A PROPOSED STANDARD EXPERIMENTAL PROCESS.*

*By F. A. Coombs, F. C. S.*

The Australian pine barks are now being used by tanners in New South Wales for the production of sole leather. These barks were described in the "*Journal of the Society of Chemical Industry,*[1]" and the present experiments were carried out to obtain results by comparative tests which would throw more light on their leather forming properties. The pine bark used (*Callitris calcarata*) contained from 20 to 25 per cent. of tannin. Two duplicate tests were carried out for comparative results. The first was pine bark against wattle bark (*Acacia pycnantha*) and the second pine bark against wattle, valonia and myrobalans as a mixed tannage.

As the hide is the most important factor in the production of leather any experiments to give good results, must be carried out in such a manner that this factor is approximately constant for the new and the standard tannage. For this experimental work sections have been cut from one hide, as shown in the following diagram. The hide is first cut into sides by following accurately the ridge which runs up the back, and then sections 2 feet square are cut from each side and numbered. Under these conditions sections 1 and 5, 2 and 6, 3 and 7, and 4 and 8 are approximately constant in area, thickness (substance) from grain to flesh and in general structure. It is assumed for this experimental process that both sides of the hide are similar in general structure, etc.

The sections were soaked, limed, delimed and tanned by suspending two pieces in upright vats, measuring 2 ft. by 2 ft. 4 in., and requiring about 32 liters of liquor to cover two sections of hide. Taking the first two sections, Nos. 1 and 5, they are both soaked, limed and delimed in the same vat at the same time: therefore both temperature, time and constituents of all liquors are constant for these two pieces until they reach the tan-liquors. Then they are separated, and No. 1 goes into the pine bark liquors, and No. 5 will go into wattle bark liquors. So that one

* *Collegium*, London Edition, 1916, pp. 205-15.

[1] Pine Barks. F. A. Coombs and A. H. Dettmann, March, 1914.

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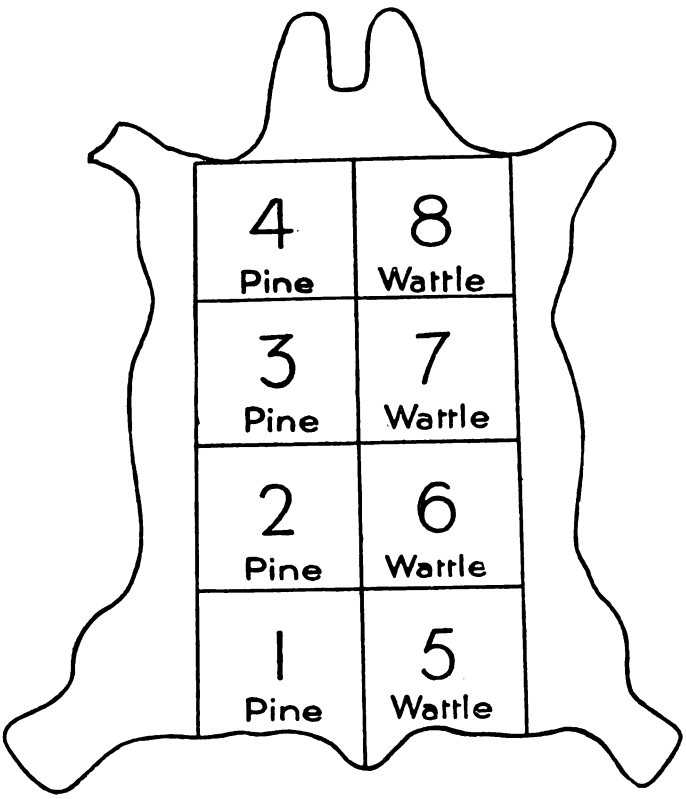
might say, that under skilled control these two sections are approximately constant until they reach the tan-liquors, and then, if any variation occurs, it will be due to a difference either in the process of tanning or in the tannin materials. In this experimental work great care has been taken to keep the tanning process approximately constant for each duplicate test so that if the hide sections be constant the variations can be traced to a difference in the tan-liquors (acidity, tannin, non-tans, etc.) or in the general structure of the tannin molecule or the molecular aggregate. What has been said of Nos. 1 and 5 applies also to the three groups, Nos. 2 and 6, 3 and 7 and 4 and 8, but it is hardly necessary to point out to practical men that No. 1 will differ from all others with the single exception of No. 5 section, and likewise No. 4 will differ with all except No. 8 section.

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The first duplicate test was carried out with Nos. 1, 2, 5, and 6 sections. The groups 1 and 5 and 2 and 6 were each placed in the limes, etc. in that order, two sections to each vat. When they reach the tan-liquors the groups are changed, and 1 and 2 are placed in the same vat with pine bark liquors and 5 and 6 will go into a vat containing wattle bark liquors. Under these conditions the two sections of hide, which are supposed to be approximately constant in structure, etc., are never separated as they pass through the various stages with the single exception of that part of the process to be investigated.

For the first test the sections were in the soaks 18 hours, limes 4½ days, water pits 2 days, deliming 1 hour, and they were then placed in the tan liquors. The limes were made up of lime and sulphide of arsenic, and the deliming solution contained 2 grams per liter of commercial lactic acid (68 per cent. lactic acid). When the pelt sections were placed in the tan-liquors they were distinctly acid on the surface with the usual alkaline streak in the center.

In the second duplicate test the sections 3, 4, 7, 8 were limed for 6 days in lime only, starting with an old lime liquor. Other factors being similar to No. 1 test until they reached the tan-liquors, and then the groups are changed, and 3 and 4 are placed in a pine liquor, and 7 and 8 go into the mixed tannage liquors. The tanning process for the first test was advanced at a constant barkometer strength for both tannages. The second was advanced at a constant tannin strength for both tannages. The time allowed for soaking and liming may appear low to tanners working in a cold climate, but in New South Wales soaking lasts for 1 to 2 days, and liming 2 to 6 days.

FIRST TEST.

| Sections 1 and 2. Pine bark liquors. | | | Sections 5 and 6. Wattle bark liquors. | | |
|---|---|---|---|---|---|
| Days | Barkometer Degrees | Lime water in cc. | Days | Barkometer Degrees | Lime water in cc. |
| 2 | 8 | 4.0 | 2 | 8 | 3.0 |
| 3 | 12 | 5.2 | 3 | 12 | 3.1 |
| 4 | 17 | 6.3 | 4 | 17 | 4.3 |
| 12 | 23 | 8.1 | 12 | 23 | 4.4 |
| 14 | 32 | 11.4 | 14 | 32 | 6.4 |
| 21 | 45 | 13.6 | 21 | 45 | 9.0 |
| 21 | 60 | 16.0 | 21 | 60 | 10.4 |

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SECOND TEST.

| Sections 3 and 4. Pine bark liquors. | | | Sections 7 and 8. Mixed liquors from 5/6 wattle bark, 1/6 myrobalans and valonia. | | |
|---|---|---|---|---|---|
| Days | Barkometer Degrees | Lime water in cc. | Days | Barkometer Degrees | Lime water in cc. |
| 2 | 9.5 | 3.4 | 2 | 11.2 | 2.8 |
| 3 | 12.8 | 5.2 | 3 | 15.2 | 3.3 |
| 6 | 16.3 | 6.0 | 6 | 20.4 | 4.2 |
| 12 | 21.4 | 8.1 | 12 | 26.0 | 5.1 |
| 14 | 32.1 | 7.6 | 14 | 36.7 | 9.6 |
| 21 | 46.3 | 12.6 | 21 | 51.5 | 10.0 |
| 21 | 51.4 | 14.8 | 21 | 60.0 | 18.7 |

1 liter of pine bark liquor at 10° Barkometer contains 20.95 grams tannin approximate.

1 liter of mixed liquors at 10° Barkometer contains 18.02 grams tannin approximate.

## LEATHER RETURNS, ETC.

The sections used in this experimental work were cut from a 55 pound green salted butcher's hide. All the sections from one side of the hide, Nos. 5, 6, 7 and 8, show a higher yield of pelt than the corresponding sections Nos. 1, 2, 3 and 4 from the other side. This result was not unexpected, because the folded hide lost more moisture from one side when it was exposed at the hide market. The process employed for this experimental work was carefully arranged to prevent an error of this description when the sections were being prepared in the lime department for the tan-liquors. Under these conditions the green weight is an unreliable factor, but the pelt weight should be approximately a constant factor for the two sections which were grouped together during the process of unhairing, etc., but after finding the percentage of hide-substance in the pelt we find that sections Nos. 5, 6, 7 and 8, which gave the higher yield in pelt also gave the higher percentage of hide-substance, which proves conclusively that the higher yield in pelt was not due to some sections being plumped higher than others, as such a result would give a lower percentage of hide-substance. Now to explain this higher percentage of hide-substance in those sections returning the higher percentage of pelt we must go back to the original green salted hide. This hide has lost moisture on one side, and has already explained, this would account for the higher percentage of pelt, and if in the process of soaking, liming, etc., these partly dry sec-

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tions were not brought back to the normal condition of the other green salted sections, then the amount of water in the pelt would be lower and the hide-substance would be higher. All tanners know there is a direct relation between the softening or the bringing back of a dry hide and the amount of water it absorbs. Under normal conditions 10 pounds of a dry hide will always return a higher pelt weight than 10 pounds of a wet salted hide, but the former will take up a lower percentage of water per pound of hide-substance, and this is probably the true explanation of the small but constant variations in the percentage of pelt weight returns on the green hide, and also the variations in the percentage of hide-substance in the pelt. Pelt weights were taken just before the sections were placed in the acid for deliming.

The leather returns calculated on the pelt weight for the first duplicate test show that a 4.3 per cent. increase of weight was obtained from the sections that were tanned in pine bark liquors, and the second test gave an increase of 7.7 per cent. for pine bark liquors. It is possible that the difference in the two sides already referred to would bring about these variations in leather returns, but this slight difference in the physical condition of the pelt might cause an excess of combined tannin on those pelt sections which contained an excess of hide-substance, and then the above results if affected by this factor would be low.

The difference in acidity of the liquors may be the cause of the higher leather returns for the pine bark tannages, and probably tanners will be surprised that the liquors for the mixed tannage did not show a higher acidity value, but this is due to the liquors being new, and they were run straight off the bark, etc., and were not allowed sufficient time to ferment, before being used. There was nothing to prevent fermentation while the leather was in the liquors, and probably the acidity increased at this stage, especially with the mixed tannage. Interesting results might have been obtained if the acidity had also been taken after the leather was removed from the liquors, but of course this would not give the amount absorbed by the pelt or leather. For both tests the pine bark liquors gave a higher acidity value, and if the affinity of hide-fiber for tannin increases directly with the increased acidity of the tan-liquors, then we must admit that part of the excess of combined tannin and the greater yield of leather from the pine bark

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tannages is due to this factor. However, this "one hide experimental process" should enable one to find out what is the value of acidity. If we take, say, similar sections of a hide and tan them with wattle bark liquors varying in such a manner that certain sections have more acid in the liquors, then all other factors being approximately constant we should get comparative results which would show approximately the value of acidity for a wattle bark tannage. Perhaps we would find that a high acidity is not a very important factor.

Paterno[2] has shown that the molecular weight of tannin is much higher with water than when glacial acetic acid is used as the solvent. In fact the difference is such that the tannin is classed as a colloid in water, and as a crystalloid in acetic acid. This is a rather interesting problem when applied to tan-liquors, and one might ask oneself how the molecular aggregate of tannin in a dilute solution compares with a molecular aggregate of tannin in a strong solution, and also what effect would the various acids in the proportion found in tan-liquors have on the tannin molecule in dilute and concentrated solutions. Probably the molecular aggregate of one distinct tannin is not constant under the above conditions. If this theory be correct we might naturally expect a smaller molecular aggregate in the dilute and acid solutions. Such a result would certainly affect our present theory of tanning. A small molecular aggregate would be expected to give a quicker and better penetration and probably a more stable leather. If the combination of the carboxyl group in the tannin molecule with the certain amino-groups in the hide-fiber be the correct theory of the combination of tannin with hide then we might state that there is a direct relation between the size of the molecular aggregate of tannin and the weight of the resulting leather.

The fats were low, and varied to a considerable extent, and as they are a weight giving factor outside of the actual tannage, the results by analysis are worked out on a leather free from fat. After the sections were tanned they were well washed in clean water and therefore the total solubles are naturally low, and it will be noted that the leather from pine bark tannages is consistently lower in water solubles than the wattle and mixed tan-

[2] *The Chemistry of Colloids*, pp. 8 and 92. V. Poschl.

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nages, therefore other factors being equal one would say that the pine bark tannage gives a more stable leather result.

| | 1st test | | | | 2nd test | | | |
|---|---|---|---|---|---|---|---|---|
| | Group | | Group | | Group | | Group | |
| Section numbers / Tannage | 1 P Per cent. | 5 W Per cent. | 2 P Per cent. | 6 W Per cent. | 3 P Per cent. | 7 M Per cent. | 4 P Per cent. | 8 M Per cent. |
| Water | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 | 14.00 |
| Ash | 0.61 | 0.52 | 0.66 | 0.25 | 0.91 | 0.34 | 0.25 | 0.36 |
| Total solubles | 11.60 | 13.84 | 10.85 | 13.02 | 9.16 | 12.76 | 11.07 | 13.79 |
| Non-tans | 1.74 | 1.94 | 1.57 | 1.75 | 1.47 | 1.96 | 1.46 | 1.83 |
| Tannin | 9.86 | 11.90 | 9.28 | 11.27 | 7.69 | 10.80 | 9.61 | 11.96 |
| Hide-substance | 39.11 | 42.05 | 40.33 | 44.54 | 38.81 | 44.19 | 38.95 | 43.25 |
| Combined tannin | 34.68 | 29.59 | 34.16 | 28.19 | 37.12 | 28.71 | 35.73 | 28.60 |
| Degree of tannage | 88.67 | 70.36 | 84.70 | 63.29 | 95.64 | 64.96 | 91.73 | 66.12 |
| $\frac{\text{Pelt weight}}{\text{Green weight}} 100$ | 109.6 | 113.8 | 116.7 | 118.9 | 115.3 | 118.4 | 135.4 | 142.0 |
| $\frac{\text{Leather weight}}{\text{Green weight}} 100$ | 73.66 | 72.7 | 74.3 | 73.36 | 69.3 | 66.5 | 67.4 | 64.5 |
| $\frac{\text{Leather weight}}{\text{Pelt weight}} 100$ | 67.21 | 63.93 | 63.63 | 61.69 | 60.1 | 56.14 | 49.8 | 45.4 |
| Percentage of hide-substance in pelt | 25.9 | 27.22 | 25.8 | 27.2 | 23.29 | 24.48 | 19.11 | 19.34 |

The combined tannin factor is all in favor of the pine bark tannage, and its relation to hide-substance is shown under the heading of the "degree of tannage." The pine bark tannins were slightly behind the other tannins in the rate of penetration into the hide. This might be explained by the theory that a greater combining affinity between hide-substance and a tannin will retard the penetration of that tannin into the center of the hide, as it must first saturate the affinity of the hide-substance for tannin on the outer part of the hide.

The leather tanned with pine bark liquors was firm and of a reddish color. Perhaps the most important factor in the actual process of tanning is the amount of tannin in the various liquors. Apparently we have had few investigators who care to tackle this problem. At the present time tanners are coloring with stronger liquors than they used, say ten or fifteen years ago. Bennett[3] states that the concentration of tannin in the early liquors will

[3] *J. S. C. I.*, 1908. This JOURNAL, 1909, page 53.

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differ for all vegetable tanning materials, and the endpoint, which shows when these liquors are too strong, will be a drawn grain. He also states that the acidity of the liquors is a factor in the increased concentration of tannin, and for his experiments with wattle bark he starts with a six, ten, and fifteen degree liquors. In New South Wales a number of sole leather tanners using this bark make their first liquor from 14 to 18 Barkometer, and while I have kept the figures for these experiments slightly above Bennett's, I am not prepared to say just what is the concentration most suitable for any tannin, as this factor will not only vary with the vegetable tannins but it will also vary with the condition of the pelt. This experimental process should enable one to test the difference in quality and weight between leather started in weak liquors and leather started in fairly strong liquors. A second experiment could be carried out dealing with the value of highly concentrated tan-liquors for the closing stages of the tanning process.

For the first test the liquors were advanced at a constant Barkometer (density) strength for both tannages, and as the pine is low in non-tannins the concentration of the tannin is higher in the pine than in the wattle liquors. However, the value of the increased concentration of tannin, as shown in this experiment, would be low, and could only be estimated by comparative tests.

WATER ABSORPTION 20° C.

| | Unrolled. | | Rolled. | |
|---|---|---|---|---|
| | Pine Section 2 Per cent. | Wattle Section 6 Per cent. | Pine Section 2 Per cent. | Wattle Section 6 Per cent. |
| ½ minute ..... | 35.6 | 45.3 | 24.0 | 23.3 |
| 1 minute ..... | 44.5 | 50.7 | 29.1 | 28.4 |
| 1¼ minutes ..... | 48.3 | 53.5 | 33.0 | 32.1 |
| 1½ minutes ..... | 50.6 | 55.2 | 35.8 | 34.4 |
| 5 minutes ..... | 52.0 | 55.7 | 38.3 | 35.6 |
| 30 minutes ..... | 53.3 | 57.0 | 40.0 | 37.3 |
| 2 hours ..... | 54.6 | 58.9 | 42.0 | 39.4 |
| 2½ hours ..... | 56.9 | 61.6 | 43.6 | 40.7 |
| 13 hours ..... | 58.3 | 64.4 | 45.6 | 43.2 |
| 32 hours ..... | 61.4 | 68.1 | 47.7 | 44.8 |

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| | Unrolled. | | Rolled. | |
|---|---|---|---|---|
| | Pine Section 4 Per cent. | Mixed Section 8 Per cent. | Pine Section 4 Per cent. | Mixed Section 8 Per cent. |
| 1 minute ..... | 21.8 | 41.1 | 23.8 | 11.6 |
| 1 minute ..... | 35.5 | 57.1 | 32.2 | 29.2 |
| 1 minute ..... | 46.7 | 67.3 | 38.4 | 35.4 |
| 1 minute ..... | 56.9 | 74.9 | 42.4 | 40.2 |
| 1 minute ..... | 62.9 | 77.5 | 46.1 | 44.2 |
| 1 minute ..... | 66.6 | 80.1 | 49.6 | 48.0 |
| 1 minute ..... | 67.9 | 81.1 | 52.6 | 51.3 |
| 5 minutes ..... | 69.7 | 82.2 | 54.8 | 54.2 |
| 20 minutes ..... | 70.6 | 84.7 | 57.2 | 56.9 |
| 23 minutes ..... | 77.6 | 92.3 | 62.0 | 62.8 |
| 32 minutes ..... | 82.9 | 94.7 | 65.0 | 67.2 |

Four sections were dried out before rolling, and they were then suspended in cold water for various periods, as shown above. The sections were in water for the time stated and then they were weighed and instantly put back again. The results are shown as the percentage of water absorbed, calculated on the air-dried leather. After the last period, 32 hours, no appreciable amount of water was absorbed. The sections were then prepared without oil and rolled in the usual manner, and when dry they were again placed in water. The results obtained before rolling show that the pine bark tannage gave a leather which offered greater resistance to the penetration of water than the other two tannages, and this result was confirmed by the "feel" and general appearance. The pine bark tanned leather did not "damp back" to that mellow state so well-known to practical men who have prepared dry leather for machine work.

After the leather was rolled one would expect that this difference between the above tannages in resisting the penetration of water would be somewhat similar to the first experiment before the leather was rolled, and this theory would probably be correct if the leather were not dried out before it was rolled, but the practical man will recognize that the leather, which was hard to damp back, would not bind together under the roller unless special precautions were taken during the damping process. These leathers were removed after the water test, exposed to the air, and when in a suitable condition they were rolled twice and finished off in the hot air drying room. If one were to take, say, the

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heavily bloomed English sole-leather and dry it out before rolling back, and without special care it would remain in a condition which one would expect to have a leather which would be hard to damp would not "bind well" under the roller and therefore there would be more air-spaces in the leather. When leather is placed in water the amount of the latter absorbed is mainly due to gravitation or water displacing air. The extent of the air-spaces would vary with such factors as acidity of liquors which would plump and open up the fiber; percentage of tannin, etc., absorbed by the hide; the condition of the leather when it is rolled; the weight of the roller; the cohesive properties of the leather after it is rolled, and the skill of the workman.

The results obtained from the leather after it was rolled show that suspension in cold water for the first test was not sufficient to bring it back to that state common to leather which has never been dried out before rolling. No figures can be supplied for the pressure under the roller, but much lower results would have been obtained if the leather had received a higher percentage of water solubles. Given a leather, which has been well rolled with air-spaces at the minimum, the best test for water-penetration is one that measures the forces usually explained under the heading of capillarity which involves a measurement of surface tension.

Under the heading of "Sole Leather Values"[4] a writer describes a number of experiments which were carried out to determine the amount of water absorbed in a given time by various leathers. The results obtained differ to a considerable extent, and the explanation advanced is that they are due to a difference in the uncontrollable factor "physical condition." The physical condition, as far as water absorption is concerned, might vary with a number of factors already described, and also with the amount of fat and finishes applied to the leather. With this experimental work an attempt has been made to control the factors in such a manner that any difference in water absorption would be due to the different leather forming properties of the materials used to tan the leather.

The amount of water absorbed by the unrolled leather is very high compared to results obtained in "Sole Leather Values," but

[4] Sole Leather Values by M. I. A. L. T. C., *L. T. Review*, Nov. 10, 1915. This JOURNAL, 1916, pp. 15-21.

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it would have been very much lower if the total solubles had been as high as, say, 25 per cent., and could be expressed as follows:

$$t_1 = \frac{w}{r} 100 \qquad t_2 = \frac{(w - x)}{(r + y)}$$

$t_1$ = The percentage of water absorbed by a leather containing a small amount of water solubles.

$t_2$ = The percentage of water absorbed by a leather containing a large amount of water solubles.

$w$ = Weight of water absorbed.

$r$ = Weight of leather.

$x$ = Water displaced by the extra amount of solubles.

$y$ = Weight of extra amount of solubles.

The rolled leather will contain less or smaller air-spaces, according to the pressure exerted by the roller, and also the physical condition of the leather. So that one might say that the high percentage of water absorbed by the rolled leather would have been lowered to a considerable extent if the leather had not been "dried out" before rolling, and also contained a greater percentage of water solubles. Then if $t_3$ represents the percentage of water absorbed by a rolled leather containing a large amount of water solubles we will have

$$t_3 = \frac{w - (x + m)}{r + y} 100$$

$m$ = the decrease in the volume of air spaces after the leather has been rolled.

After carrying out the above experiments I feel quite satisfied that the pine bark tannins produce the better water resisting leather, and the best test is one which may not appeal to the chemist with no practical experience. If one takes two sections of dry leather, which vary only in the tannin materials used for the tanning process, and place them in water, one will generally recognize a difference in the "feel" and one leather may become much softer than the other. Such a change in the physical condition is known to be directly due to the inferior water resisting properties of the leather. If these two sections be rolled the soft pliable one will be more compressed and leave a smaller number of air spaces. Now place the dry rolled leather in water, and what we have described as the softer leather will take up in the

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early stages the smaller amount of water, owing to a smaller amount of air spaces, but as shown with sections 4 and 8 after rolling, another factor may be introduced, and that is tendency of the leather to swell in water after rolling, and this would be at its maximum with a leather which absorbs water freely as represented by the soft pliable state mentioned above.

The members of the International Association gave a considerable amount of their time to improving a method for the analysis of tannin materials, and I think that they should now adopt a standard experimental process for tanning heavy leathers. The process which I have described has been used at the Sydney Technical College for illustrating various tannages, and also certain factors, such as plumping with sulphuric acid, etc. It should be a decided aid to tanners who wish to experiment with tannin materials before using them on a large scale, or if they wish to change their present process or investigate new theories.

Leather Trades Chemists who are asked to report on new theories, patent processes, etc., can use this "one hide experimental process" in the following manner. It was claimed by certain persons in N. S. Wales that they had a process of tanning in *vacuo* that gave results in four weeks which were superior to results obtained by the normal process after being in the tan pits three months. To test this theory[5] a hide was cut into sections as described for the "one hide experimental process," and the sections were dehaired, etc. When they were ready for the tan-liquors one section of each of the four groups was sent out to the tannery to be tanned by the vacuum process, and the remaining four pieces were tanned by the normal process at the Sydney Technical College. The results obtained, largely a matter of weight returns, were not in accordance with the above claim.

A considerable amount of energy and time has been spent in examining qualitative tannin tests so that various tannin materials could be detected when they are mixed, such as mangrove in quebracho extract. If the leather trades chemists are ever going to get the bottom of the vegetable tannin process they must adopt an experimental process which is a miniature reproduction of the commercial process, and then they will deal with extracts, etc., directly from the standpoint of their leather-forming properties,

[5] Report to Department of Public Instruction, June, 1913.

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not caring what particular tannin the extract contains, so long as it is capable of returning a good leather.

While one must admit that qualitative tests, which indicate the presence of various tannins, are very useful, still the fact remains that the leather-forming properties of the various tannins in mixed tannages have never been standardized, and therefore, if we were in the position to detect the various tannins in one extract we are not in the position to say how these tannins would affect the quality of say sole-leather.

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## THE ESTIMATION OF SULPHIDE IN LIME LIQUORS.*

*By Hugh Garner Bennett, M. Sc.*

The re-publication in the London Edition of the *Collegium* [1916, p. 191] of the article[1] of McCandlish and Wilson from the *Collegium* of August, 1914 (which issue has not yet been received by British Chemists), re-opens the question of determining sulphide in lime liquors.

### The Zinc Method.

(1) *Error Due to Precipitation of Zinc Hydrate.*—In their first paper McCandlish and Wilson criticise the zinc sulphate-ammonium chloride reagent because it has no ammonia in it, pointing out that this ammonia is necessary to retain zinc hydrate in solution, and to prevent the loss of sulphide as hydrogen sulphide. No one will doubt this view being correct. If the reagent contains 5 per cent. ammonium chloride only, the process will not work at all. Thus, if this reagent be used to titrate 50 cc. clear saturated lime water, a precipitate of zinc hydrate forms, increases and then decreases, but is not re-dissolved even by 25 cc. of this reagent. The use of ammonium chloride only, is simply out of the question. In the words of McCandlish and Wilson "it does not contain sufficient ammonia" for use with lime solutions.

The obvious alternative is to add ammonia, as well as its chloride until there is sufficient to keep the zinc hydrate in solution.

* *Collegium*, London Edition, 1916, pp. 219-23.

[1] This paper was published in this JOURNAL, May, 1914, and attention was called to it in a footnote on p. 110. of the March 1916 number in which Mr. Bennett's paper was reprinted.—ED.

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Now it is clear that however much ammonia and ammonium chloride are used in making up the reagent, the first additions in titration deliver only small amounts of ammonia and ammonium chloride into the lime liquor. Hence, however strong the reagent is made in ammonia and ammonium chloride, there will be some precipitation of zinc hydrate at first, and the titration will be unreliable until sufficient ammonia and ammonium chloride have been added to re-dissolve the zinc hydrate. When this stage is reached, this particular source of error may be ignored.

If the standard zinc solution be made up as suggested by the writer in *Collegium,* 1915, p. 314 (This J., 1916, p. 112), then 50 cc. clear saturated lime water require 3.5 cc. nearly, of reagent to re-dissolve the zinc hydrate first precipitated. Any titrations of 50 cc. lime liquor in which less than 3.5 cc. reagent are used will be unreliable, but if more than 3.5 cc. are required, the estimation of sulphide may be accepted so far as this particular source of error is concerned.

There are, however, several other points which should be noted.

(a) The amount of lime liquor taken for titration is an important point. If a large volume be taken, a much bigger titration is necessary to add the requisite amount of ammonia and ammonium chloride. In many factories at least 50 cc. lime liquor would have to be taken in order to obtain a titration of reasonable size. Hence, if the reagent be made up as suggested in *Collegium,* 1915, p. 314, at least 3.5 cc. reagent must be used.

(b) Lime liquors vary somewhat widely in their sulphide contents, and for some liquors containing small amounts of sulphide, it might be advantageous to use more ammonium chloride in making up the reagent, and in some cases, possibly more ammonia also. In that way the zinc hydrate would be kept in solution for even smaller titrations. The reagent indeed may be adjusted in any sense, according to the nature of the lime liquors which are being tested. The reagent suggested by the writer, (*Collegium,* 1915, p. 314) is suitable for liquors containing from 0.1 per cent. to 1.0 per cent. of sodium sulphide crystals.

(c) The precipitation of zinc hydrate in the case of a used lime liquor is even less likely than in the case of pure lime water, because of the free ammonia, and ammonium salts which

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are invariably present in such liquors. The zinc hydrate will be the sooner re-dissolved, and the smaller titrations the more reliable.

(d) The zinc method can never be very suitable for estimating small amounts of sulphide (*e. g.*, 0.1 per cent. and less), because (i) the volume taken for titration is limited by the necessity of keeping the zinc hydrate in solution, and (ii) the end points (whether by nitro-prusside, lead, or even nickel) is poor if the titration be small, leading to large percentage errors. This latter point has been previously mentioned by the writer (*Collegium*, 1915, p. 316), and an alternative method was given for such liquors.

(e) One cannot accept the statement of McCandlish and Wilson that the solution containing both ammonia and ammonium chloride has "no practical advantage over the one containing no ammonia." There is a very real advantage, *viz.*, that containing no ammonia is utterly unworkable, whilst that containing both ammonia and ammonium chloride is quite workable when the conditions are correct, *i. e.*, when the amounts of ammonia and its chloride added during titration is sufficient to insure no precipitate of zinc hydrate at the point where the titration is finished.

(f) Messrs. McCandlish and Wilson anticipated the writer in pointing out that the amount of water used in dissolving the zinc sulphate influences the amount of ammonia used to re-dissolve the zinc hydrate. It may be further pointed out, however, in this connection (i) that one is very liable to use so much water that no amount of concentrated ammonia will ever re-dissolve the precipitate, and (ii) that even if one succeeds in re-dissolving the precipitate in excess of ammonia, it is very often re-precipitated on dilution, when making the liquor up to mark. The reagent containing ammonia only is not easy to make. Some have even said it is impossible to make.

One cannot but conclude that from the standpoint of keeping zinc hydrate in solution, the use of both ammonia and ammonium chloride is a distinct improvement on attempting to use either alone.

(2) *Error Due to Suppression of Zinc Ions.*—It has been pointed out by McCandlish and Wilson, that too great an excess of ammonia (when used alone) converts zinc ions into the com-

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plex ion $Zn(NH_3)_4^{..}$, and so gives abnormal results owing to the non-precipitation of zinc sulphide. Whatever amount of ammonia be used, some zinc ions will be thus removed, and McCandlish and Wilson conclude that "with all concentrations we are sure to obtain abnormal results with limewater." Messrs. Blockey and Mehd have admitted this source of error, and McCandlish and Wilson in their recently re-published paper again insist on this error, even when both ammonia and ammonium chloride are used, and quote Blockey and Mehd in confirmation.

It appears to the writer, however, that this error is negligible for all practical purposes if the reagent be made up as suggested in *Collegium*, 1915, p. 314. Several reasons may be advanced.

(a) The use of ammonium chloride permits such a reduced quantity of ammonia to be used that this error is greatly minimized. McCandlish and Wilson favor the solution[1] made with ammonia only with "just enough ammonia to prevent the precipitation of zinc hydrate" so that "only a minimum error will result from the removal of free Zn ions." The reagent favored by the writer, however (containing 25 cc. concentrated ammonia and 50 grams ammonium chloride per liter), does not contain sufficient ammonia to re-dissolve the zinc hydrate without the assistance of the ammonium chloride. Any error due to zinc ammonia complexes must therefore be distinctly less with this solution than with the solution favored by McCandlish and Wilson. The use of ammonium chloride, as suggested by Blockey and Mehd, is thus a great advantage in that it permits a much smaller quantity of ammonia to be used, and so reduces any possibility of error due to excess of ammonia. It is true that Blockey and Mehd did not advance this point as an advantage of their suggested reagent, but it is, nevertheless, a very important point.

(b) Further, the use of ammonium chloride in addition to ammonia, is of value in yielding complete precipitation of zinc sulphide. It has long been known that the presence of ammonium chloride assists in this direction. In the gravimetric estimation of zinc as sulphide, for example, a moderate amount of ammonium chloride is always added before the zinc sulphide is

[1] Unfortunately these authors give no details as to how this solution should be made and what amounts of ammonia should be used.

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precipitated. That zinc can be estimated successfully under these conditions indicates that the precipitation is complete. There seems no reason to suppose that this precipitation is much less complete in the volumetric process under discussion.

(c) Whilst it is doubtless true that zinc-ammonia complexes are formed which do not react with sulphide, these complex ions are in equilibrium with ammonia and free zinc ions. This equilibrium is disturbed by a partial precipitation of zinc sulphide, owing to the removal of zinc ions. More zinc ions are then formed at the expense of the zinc-ammonia complex, which are in turn removed by precipitation. This process is repeated until the precipitation of zinc is practically complete.

If, with these points in mind, McCandlish and Wilson are still of the opinion that the ammonia and ammonium chloride reagent yields abnormal results, owing to the non-precipitation of zinc sulphide, it is for them to indicate the extent of the error in lime liquors of any particular strength in sulphide, but especially in those containing from 0.1 to 1.0 per cent. sodium sulphide crystals, such as exist in many factories.

Only one further point remains to be mentioned in this connection. If a method of analysis estimates 0.11 per cent. of sulphide when there is only 0.1 per cent., it may be true from one point of view to say the error is 10 per cent., but it is equally true from another point of view to say that the error is only 0.01 per cent., and that the method is therefore sufficiently accurate for the purpose in view.

In any case one cannot but conclude that from the standpoint of the complete precipitation of zinc sulphide, the use of both ammonia and ammonium chloride is a great improvement on the use of ammonia alone, and from any point of view is indeed *a much greater improvement than Blockey and Mehd ever claimed it to be, if the ammonia does not exceed 25 cc. concentrated ammonia per litre.*

### The Copper Method.

In the very brief abstract of the second paper of McCandlish and Wilson, which appeared in *J. S. C. I.*, 1914, p. 606 the copper method was suggested provisionally.

It may be pointed out that it is hardly likely that this principle

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is capable of successful application, as the copper-sulphide precipitate is not cupric sulphide as they assume, but a mixture of cupric and cuprous sulphides. In solutions without organic matter the composition of the precipitate corresponds approximately to the formula $Cu_4S_3$. Hence, in estimating copper as sulphide gravimetrically, it is necessary to convert this precipitate entirely into cuprous sulphide by heating with sulphur in a stream of hydrogen before it is weighed. In the case of used lime liquors, which contain organic reducing agents, the proportion of cupric and cuprous sulphides is likely to be even more irregular. Hence, in the method of McCandlish and Wilson, whether the excess of copper be estimated colorimetrically or in any other way, the amount of copper precipitated bears no stoichiometric relation to the sulphide in the lime.

### The Cadmium Method.

Another method of estimating sulphide in lime liquors has been recently suggested by Helfrich (This J., Vol. X, p. 401). This consists in precipitating the sulphide as cadmium sulphide in acetic acid solution, washing the precipitate, dissolving it in hydrochloric acid and titrating the hydrogen sulphide with iodine.

It is clear that this method must suffer from the same disadvantage as if cadmium were not used at all, *i. e.*, as if the lime liquor were simply acidified with hydrochloric acid and titrated with iodine direct. The objection is that iodine will be consumed in oxidizing organic matter. The precipitation as cadmium sulphide will doubtless diminish this error, but will hardly eliminate it, for the cadmium chloride and acetic acid will certainly precipitate along with the sulphide a considerable amount of organic matter held in solution by the lime.

It may be that for liquors containing fairly large amounts of sulphide and little dissolved hide substance, the error is relatively small, and the process therefore useful for control work, but it is clear that for liquors containing small amounts of sulphide, the results are likely to be very unreliable.

### The Arsenic Method for Control Work.

In cases where large amounts of sulphide are used, in conjunction with clean liquors, a rapid method for control work is

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often of great service. A very handy process for this purpose is an abridged form of the arsenic method previously suggested by the author for accurate work, *"Collegium,"* 1915, p. 315. In this rough abridged method the distillation is omitted, and the process carried out as follows:

Into a flask 100 cc. settled lime liquor, and afterwards 40 cc. (say) of alkaline arsenite solution are pipetted. When well-mixed, 10 cc. (say) of concentrated hydrochloric acid are added, making a total volume of 150 cc. (say) and a liquor acid to methyl orange. The sulphide is precipitated as arsenious sulphide along with much organic matter. The liquor is filtered and an aliquot portion of the filtrate is pipetted into a conical flask for titration with N/10 iodine solution. Before the titration is commenced this liquor is made alkaline again to methyl orange by the addition of a saturated solution of sodium bicarbonate, or even of the solid bicarbonate itself.

This method is open to the same criticism as the cadmium method, *viz:* that organic matter is present in the liquor, being titrated with iodine, and that some iodine will be consumed by it. Hence, it is only suggested for control work where the error is known to be relatively small. It will be found much more convenient than the cadmium method for such a purpose, because there is no need to heat the liquor, in order to precipitate the sulphide, and the tedious washing of the precipitate is also avoided. Needless to say the amount of N/10 alkali arsenite used must be adjusted according to the approximate amount of sulphide present. Control work with this method can always be easily checked when necessary by the full arsenic method, including distillation, as previously described.

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## ABSTRACTS.

**Sumac Cultivation in Sicily.** CONSUL SAMUEL H. SHANK, Palermo, Italy, in *Commerce Reports.* There are two species of sumac grown in Sicily, the wild and the cultivated. The wild variety has a short stalk, small leaves attached two by two to a short stem, the leaves sparse covered with a white fuzz on both sides, the stem with no small leaves near its base. The cultivated plant (*Rhus coriaria*) has a longer stem than the wild, its leaves are larger and are covered with fuzz only on the lower side, and the stem of the leaf has small leaves along its entire length.

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Sumac requires a dry, loose soil. The best is a clay soil with lime and silica mixed. It does not grow well in damp, compact ground. The soil may be rich or poor, so long as it is dry. However, the best sumac is grown on soil of volcanic origin. This soil, together with much heat, produces the greatest amount of tannin. The heat is perhaps the most important element in the production of tannin. In Sicily sumac is grown at all elevations up to 2,000 feet. Sumac is planted in furrows 8 inches wide, 6 inches deep, and 27 inches apart, the plants being placed 27 inches apart in the furrow. The sprouts should be taken from a full-grown plant and care exercised that the roots are entire. They must be a year old. The planting is usually done in December or January. The ground should be plowed twice about four to six months previous to the planting. The plants should be cut down to within 6 inches of the ground. During the first year the ground should be spaded six times, immediately after the planting, in February, April, May, June, and September. The first three spadings should be deep, the others only light. During the second year there should be three spadings, in January, March, and May. In December the little shoots that have appeared at the foot of the plant should be cut off. Sumac should be cultivated alone. The shade of trees retards development and reduces the amount of tannin. The gathering of the leaves takes place when they commence to turn yellow, usually in July and August. Some growers cut the twigs off near the stem and send them in this form to the thrashing floor, where the leaves are separated from the stems by beating or by thrashing with horses. However, this is not a desirable method, as it does not produce a good quality. The best method is to gather the crop in three periods. First the leaves near the stalk up to about the middle of the limb are gathered. Twenty or twenty-five days later half of the remaining leaves are gathered. A few days after this the ends of the twigs are cut off. This method gives two or three qualities of sumac, but as it requires a great deal of time and labor, the usual method is to cut off the whole plant near the ground. The twigs are piled on a floor and are turned three or four times a day with a fork. After the leaves are separated from the wood they are taken to the mill, where they are packed in bales or ground for shipment. There is no treatment at the mill which affects the amount of tannin contained in the sumac.

**Vegetable Tanning Colloids—Theory of Their Combination and Action on a Chemical-Colloid Basis.** W. MOELLER. *Collegium*, 548, 441-57 (1915); 549, 1-16; 550, 43-50 (1916). In all tanning materials there are present two substances, a peptizer and a peptizable substance, either of which is sometimes almost, but never entirely, pure. Among the vegetable tans, the tannins are the peptizers, the ellagic acids and catechin-phlobaphenes the peptizable substances. Tannin is always recognizable in all pyrogallol and mixed pyrogallol-catechin tans, but is not recognizable in the pure pyrocatechin tans by chemical means. But the colloid behavior of these bodies reveals its presence, in complex combinations with the peptized

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bodies. Solutions of pure tannin are but slightly colloid, are freely dialyzable, and form colloid solutions with gelatine in all proportions. This colloid property shows that it is impure, these properties being attributable to the impurities. Pure tannin is unknown since the complex combination of peptizer and peptized substance is not decomposed by ordinary chemical reactions. When other pyrogallol-containing substances than gall-nuts are treated by the process for obtaining tannin used with gall-nuts, the products, usually considered as pure tannin, are not necessarily so, but all contain the same amounts of impurities, since all these substances, along with large amounts of tannin, contain varying small amounts of colloid ellagic acid—non-tans—and the process gives the same ultimate product with all. Tannin is known as a protective colloid in many relations, as in colloid solutions of Au, graphite, etc. Ellagic acid and phlobaphenes are not substances split off from tannin, but exist ready formed in the plants, where they may arise from the tannin by condensation with splitting off of pentoses or hexoses, are peptized by the tannin in extraction, and subsequently deposited by changes in the colloidal equilibrium of the extract. When any pyrogallol solution is boiled some tannin is changed to gallic acid, thus removing a part of the peptizer, and the ellagic acid is precipitated, partly pure, in crystals, partly amorphous, and containing the peptized complex. Catechin and phlobaphene bear the same mutual relation as crystalline and amorphous ellagic acid. The first is a product ready formed in the plant, which is peptized in extraction, and deposited as amorphous phlobaphene when the colloidal equilibrium is altered. The great numbers of different phlobaphenes represent products obtained by different degrees of peptization, and consist of varying proportions of catechin and peptizer in combination. Ellagic acid, catechin, and its isomeric polymers, the phlobaphenes, together with the resins and dyes which occur in all vegetable tanning substances, are "iso-colloids." When a pyrogallol tan is dissolved in acetone, the crystalline ellagic acid is in true, the ellagic phlobaphene in colloidal solution. Von Weimarn's theory of the crystallization of colloids applies to the mineral tanning substances without any difficulty, but not so readily to the vegetable ones. When any strength of any vegetable tanning solutions are diluted 500 to 800 times, the first separation form, microscopic, of both pyrogallol and pyro-catechin peptized substance is in the form of droplets, gradually changing either to coarse crystals or to amorphous forms. The colloid has been in the liquid in the form of droplets, *i. e.*, an emulsion, with which its properties closely agree. These droplets, as in all colloid dispersions, have a core of unpeptized substance, and a hull, composed of a complex compound of peptized substance and peptizer, the former either phlobaphene or ellagic acid, both of which, in crystalline, rather in monomeric form, are also found in true solution. In the tanning process the peptizer, *i. e.*, the tannin, forms a solid solution with the hide fiber, but does not tan it. The surface of the fiber is a semi-permeable membrane, through which the amorphous colloid cannot pass, therefore the peptizer

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is withdrawn from the compound on the surface of the droplets, by dialysis, and the freed peptized substance is deposited upon the surface of the fibers, where it unites, by condensation, along with the particles of the core, and ultimately becomes crystalline. This is in the ideal case of the complete soluble condition of the peptizable material. In general, especially in mineral tanning, there is either an excess of peptizer, when the peptizable substance is in true solution; or of the latter, when it is in the form of an emulsion. In the first case, the dissolved compound of peptizable material would be hydrolyzed by dialysis, then an intermediate peptization on the surface of the fiber would occur, and, after the critical stage passes, condensation as explained above. But the tanning effect, as in the case of pure gall-nuts, would be small, because of the small amount of peptized substance. When there is a suspension, as in the second case, the amount of peptizer to be dissolved in the fiber is relatively small, and the relatively large amount of peptizable substance deposited and crystallized on the outside would constitute the tanning. M. considers also the influence of soluble and insoluble non-tans, in the light of his theory. Although they have an influence, their presence is not necessary.

W. B. J.

**Mangrove Supplies in Porto Rico.** HARWOOD HULL, Correspondent, San Juan, in *Commerce Reports.* Mangrove grows in sea water in marshes along the coast of Porto Rico, and in many places is abundant. There are several varieties, called by different names, some of which are sources of tannic acid. Although the bark is sometimes used locally in tanning processes, so far as can be learned there has never been any attempt to make Porto Rico mangrove a source of commercial tannic acid. One variety of mangrove, generally known here as "mangle zapatero," or "shoemaker's mangle," is considered to be the best variety for tanning and dyeing, and the extracted juice may also be used to neutralize the effect of salt water used in steam boilers. Frequently quantities of bark are thrown into a boiler to prevent "caking" on the pipes. All of the varieties of mangrove grow slowly and the "mangle zapatero" produces a knotty, brittle wood. Two other varieties, known as "chifle de vaca" and "botoncillo," produce a tough, fairly straight wood, free from knots, which is believed to be suitable for tool handles or spokes for carriages and other vehicles. Although this product has never been marketed, a price of $65 to $70 per ton, f. o. b. port of Mayaguez, P. R., has been quoted, packing either in sacks or otherwise, for the account of the purchaser. For the wood itself, cut in 2-foot lengths and air dried, a process which requires approximately two weeks, a price of $1.25 per hundred pieces has been quoted. It is probable that these prices could be lowered for large orders for contract delivery and after persons had an opportunity to become familiar with the preparation of either the wood or the bark. The supply should be abundant and constant. Three samples of "mangle zapatero" are sent from the following districts: La Pitahaya, Lajas, P. R.; La Palguera, Lajas, P. R.; Puerto Real, Cabo Rojo, P. R.

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The following samples are also sent: "Mangle chifle de vaca," from Puerto Real, Cabo Rojo, P. R. (not seasoned); "mangle botoncillo," Puerto Real, Cabo Rojo, P. R. (not seasoned); "mangle botoncillo," from La Palguera, Lajas, P. R. (seasoned). The samples mentioned may be inspected at the Bureau of Foreign and Domestic Commerce or its district offices. Refer to file No. 1039.

**The Drying of Leather.** CHARLES P. FREY. *Hide and Leather*, Oct. 7, 1916. A cubic foot of dry air at 80° F. can take up about 0.001 pound of water vapor. Thus 1,000 cubic feet are necessary to take up 1 pound of water, or from 8,000 to 10,000 cubic feet to dry one side of leather. If the air is moist instead of dry, the quantity necessary will be proportionately greater. At 104° F. the capacity of air for moisture is about twice as great as at 80°, so that only half as much air would be necessary to absorb a given amount of water.

**Used for Spent Tanbark.** *Hide and Leather*, Oct. 7. The Forest Products Laboratory has developed a process which is now being operated commercially by which 20 to 30 per cent. of bark is incorporated with other fiber in the manufacture of roofing felt, the product being entirely satisfactory. A good grade of wall paper has been produced, containing 80 per cent. spent bark, and another company is making fiber conduits of this material. Other uses have been suggested, including the manufacture of wall board, bottle wrappers, sheathing paper, deadening felt and carpet lining.

**Valonia.** ANONYMOUS in *S. and L. Rep.*, Sept. 21, 1916. Valonia comes chiefly from Greece and Asia Minor. Valonia liquors tan slowly. For making heavy leather it does not pay to get the highest grades of cups, as the higher price is commanded only because of a slightly superior color. Greek valonia is regarded as inferior to Turkish. Valonia tannin belongs to the pyrogallol class. Liquors made from it deposit ellagic acid or "bloom" on standing. This property is perhaps best utilized by using it as a "dusting" material. Valonia produces leather of a light color, and this color is more permanent than light shades produced by some other materials.

**Artificial Leather.** *Hide and Leather*, Oct. 21. Britain finds a way to "help" tanning industry. That Germany is not the only belligerent country that has devised new means of meeting the exigencies of war is shown in a report from Consul Claiborne of Bradford, Eng., who says that English manufacturers have found many ways of providing articles made extremely scarce because of war demands. One of the interesting substitutes is artificial leather. Linen duck is coated with varnish to which is added a small quantity of siccative and Venetian red. Several layers of the dried linen are then joined together in sheets of varying thickness. The adhesive mixture used for this purpose consists of four parts of heated wood tar pitch, with the addition, during constant stirring, of two

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parts of India rubber dissolved in benzol, four parts of Venetian red, mixed to a thick consistency with French turpentine oil, and two parts of cork powder. Sheets thus prepared are compressed between powerful rollers. The product, it is claimed, serves as an excellent substitute for leather, especially for the soles of footwear. It can be easily sewn and pegged, and can replace leather in many of its uses.

**Exports and Prices of Cow and Buffalo Hides.** CONSUL E. S. CUNNINGHAM, Hankow, China, in *Commerce Reports*, Nov. 1. In 1915 the quantity of cowhides exported amounted to 4,578,667 pounds in excess of the exports of the preceding year. The hide season began three months before the opening of the year. In January, 1915, there was a slight decline in prices as compared with the preceding year. They opened in January at about 27 cents gold per pound for primes. This continued with little change until the close of the year, although in May there was a reduction to about 25 cents and in October the price reached 36 cents, owing to the increased demand, not only from the United States, but from France, and particularly Italy. In December the price again declined to about 32 cents, due to Italy having received its requirements. The shipments during 1915 were to the same countries as before, omitting, of course, Germany, although the United States took more than it had been accustomed to do from this market. Buffalo hides were not shipped to the United States to any considerable extent prior to 1915. While the shipments have been small, they were sufficient to justify the local exporter to consider it as a potential market. The prices on the local market were about the same at the close of the year as at the beginning, though they increased 15 per cent. about July.

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## THE DETERMINATION OF ALKALINE SULPHIDES, III.

*By Douglas McCandlish and John Arthur Wilson.*

The problem of determining accurately the amount of sulphide in lime liquors has never been solved to the satisfaction of all concerned. Earlier comments by the authors[1] are criticised by Mr. H. G. Bennett,[2] who contests the statement that a standard zinc sulphate solution containing both ammonia and ammonium chloride has no practical advantage over one containing only ammonium chloride for the estimation of sulphides *in lime solutions*. In titrating aqueous solutions of sodium sulphide with standard zinc sulphate solutions, using sodium nitroprusside as external indicator, the presence of ammonia is of advantage in preventing hydrolysis of the sulphide with the formation of hydrogen sulphide, which does not produce a color with the indicator. The presence of sufficient ammonia will prevent the precipitation of zinc hydrate by lime solutions, but this is no proof that the addition of ammonia will give a lesser error. This will be made clearer by theoretical considerations.

The real difficulty with the zinc method lies in the fact that zinc hydrate is even less soluble than zinc sulphide. As a matter of fact the method would be practically impossible were it not for the greater degree of ionization of zinc hydrate. Consider a titration nearing its end-point; the solution is saturated with zinc sulphide and therefore

$$[Zn^{++}] \times [S''] = K_1 \text{ (the solubility-product constant}^3\text{)}.$$

From the law of mass action

$$[Zn^{++}] \times [OH']^2 = K_2[Zn(OH')_2].$$

Solving the two equations simultaneously,

$$[S''] = \frac{K_1[OH']^2}{K_2[Zn(OH)_2]}.$$

In order that an end-point may be reached [S''] must decrease, but its value cannot become less than the above equation will permit. The lowest value of the right hand member, for a given

[1] This JOURNAL, 1913, p. 28, and 1914, p. 203.

[2] *Collegium*, London Edition, 1916, p. 219; This JOURNAL, 1916, p. 585.

[3] See Qualitative Analysis, Part I, p. 141, by Julius Stieglitz (Century Co., New York).

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hydroxyl concentration, is obtained when $[Zn(OH)_2]$ has its greatest value, which would be obtained only by zinc hydrate being present to saturation, giving $[Zn(OH)_2]$ a fixed value, whence the value of the right hand member becomes expressible by $K_3[OH']^2$, the lowest value which [S″] can assume. But when [S″] has reached this value, any further addition of zinc ions must result in the precipitation of both zinc sulphide and zinc hydrate in such proportion as to satisfy continually the equation

$$[S''] = K_3[OH']^2.$$

This reasoning is not concerned with the presence or absence of ammonia in the liquor and therefore should hold true regardless of whether or not ammonia has been added to the standard zinc sulphate solution. The practical significance of the reasoning depends upon the order of magnitude of $K_3$, but it is unnecessary from a practical standpoint to determine it, since all of the information desired can be obtained by titrating aliquot portions of a given lime-sulphide solution with standard solutions of zinc sulphate and ammonium chloride both with and without ammonia. We prepared two standard solutions, one of N/10 $ZnSO_4$ containing 50 grams per liter of ammonium chloride, the other exactly the same excepting that it contained in addition 25 cc. per liter of concentrated ammonia. Titrating 50 cc. of lime-sulphide solutions which required from 1.0 cc. to 9.0 cc. of zinc reagent, using a 0.2 per cent. sodium nitroprusside solution as indicator, we found that the two standard solutions gave very little difference in result. That containing ammonia gave slightly higher titrations, due no doubt to the retention of a very small amount of zinc in solution as zinc ammonium ions, since the final titration can be increased almost indefinitely by adding increasing quantities of ammonia. Mr. Bennett finds, on the other hand, that the solution containing no ammonia "is utterly unworkable." The titrations are easy to perform so that anyone interested can easily satisfy himself as to the point under discussion. As a further confirmation of the reasoning we prepared two more solutions, one of N/10 $ZnSO_4$ alone, the other of N/10 $ZnSO_4$ containing 40 cc. of concentrated ammonia per liter. The one containing ammonia gave only slightly higher results than the other,

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but both gave considerably higher results than the solutions containing ammonium chloride. It is of course obvious that where the conditions are such as to bring the alkalinity of the liquor very near to the neutral point, the presence of ammonia will be of value in preventing hydrolysis of the sulphide with consequent loss of hydrogen sulphide.

From the above equations it will be readily seen that the amount of error must increase with increasing hydroxyl-ion concentration. This is easily tested and found to hold true by adding sodium hydrate to the liquor to be titrated. The real value of the ammonium chloride, in making determinations where no correction is made for the precipitation of zinc hydrate, lies in its reducing the concentration of hydroxyl ions, which it does to a very considerable extent. The equations show also, since the lime is of limited solubility and is usually present to saturation, that the *absolute* error will increase but little as the concentration of sulphide is increased, making the *percentage* of error grow considerably smaller.

But in the stronger solutions a difficulty arises, which we mentioned in our first paper on this subject, namely, that the precipitated zinc sulphide, which is carried with the solution to the spot plate, continues to give a coloration with the nitroprusside indicator, even after the zinc sulphate has been added in excess. The error from this source is avoided by working with solutions of low sulphide concentration, which is one reason why we have confined our work particularly to such solutions. However, in the opinion of the authors, a method should not be called satisfactory which is unreliable for solutions containing less than 0.1 per cent. of sodium sulphide crystals, which is more than 16 pounds in a vat of 2,000 gallons of water (20 pounds per 2,000 Imperial gallons). This is especially true in view of the fact that in many tanneries, not only are liquors of such strengths employed but it is the determination of sulphide in the *used* liquors that is of chief importance.

The discussion of the various zinc sulphate, ammonia and ammonium chloride solutions contained in our first paper was not intended to convey the impression of our favoring any one of these solutions. That we appreciated the deficiencies of all of them is indicated by our concluding remark in that paper that

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"neither the addition of ammonium chloride nor of ammonia to zinc sulphate furnishes a solution which gives correct results under all conditions."

In spite of these defects the zinc method is probably the most convenient method for estimating sulphides in lime liquors which we possess at the present time, but it is well to appreciate its limitations, which are sufficiently serious to demand either improvement or else the devising of some better method.

The copper method in its present form is not so satisfactory as the zinc method, but has a great advantage in that it eliminates the trouble due to alkalinity of the liquors and possibly may be developed into a more rapid method than the latter. Either needs perfecting to be entirely satisfactory; it is a question of which offers the greater possibilities. The principle of the copper method is the addition to the lime liquor of an excess of a standard solution of acid and some metal of the $H_2S$ group, filtering, determining the amount of metal salt still remaining in the solution, and calculating the concentration of sulphide in the original liquor from the loss in concentration of metal. Satisfactory results were obtained in some cases by using standard copper sulphate and acid and determining the excess of copper colorimetrically after addition of ammonia. In other cases, however, it was almost impossible to match the colors because of carbonation of the cuprammonium hydroxide or because of the presence of ammonia in the solution of concentration different from that in the standard.

Mr. Bennett contends that it is hardly likely that the principle of the method is capable of successful application because the precipitate is not cupric sulphide but a mixture of cupric and cuprous sulphides. Some authors hold the view that the action of $H_2S$ upon copper sulphate in acid solution is as follows:

$$4CuSO_4 + 4H_2S = 2CuS + Cu_2S + S + 4H_2SO_4.$$

But even if this represented the action in the method under discussion, we fail to see how it is thus rendered incapable of successful application. In the above equation the amount of copper precipitated is as much a direct measure of the sulphide in the original liquor as though the precipitate were cupric sulphide alone, and it is only with the *excess* of copper sulphate that we

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are concerned. More pertinent to the method is a statement by H. W. Schimpf[4] who says that when sodium sulphide is added to an acid solution of cupric sulphate the precipitate is *invariably* CuS. Sutton[5] also uses this principle for the estimation of copper in acid solution by titration with an alkaline sulphide. These facts together with our actual experiments do not support Mr. Bennett's statement that the amount of copper precipitated bears no stoichiometric relation to the sulphide in the lime.

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## THE SOAKING OF SKINS.*

*By M. C. Lamb, F. C. S.,*
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Soaking is the first essential operation preliminary to the manufacture of all classes of leathers; it may be said to be the foundation upon which good leather is built, for if it is indifferently performed the finished product will be inferior.

Lord Allerton, who was Great Britain's most up-to-date tanner some thirty years ago, has often been quoted as stating that "Good leather was made in the limes;" thereby emphasizing the importance he placed on the proper depilation of goods before commencing the tannage. It might equally truthfully be said that "Good leather is made in the soaks." Soaking is all essential to the liming process; if skins are insufficiently soaked the liming process can never be thorough.

The primary object to be attained by this operation is the separation of the fibers which in the case of dry and "dry salted" goods particularly, have become cemented together by the partial liquefaction of the gelatinous matter of the skin, during the process of drying. Unless these fibers are brought back in the soaking process to as nearly as possible the same soft pliable condition in which they existed in the warm skin as removed from the butchered animal, the liming process is either unduly prolonged by becoming a supplementary soaking process, or is incomplete when the goods are removed.

[4] Volumetric Analysis, p. 363. (John Wiley & Sons).

[5] Volumetric Analysis, p. 207. (Blakiston).

* *S. & L. Rep.*, Oct. 19, 1916, under the title "Modern Methods of Leather Manufacture."

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The process under discussion is without doubt one of the most neglected of all the operations necessary to the conversion of raw skins into leather, due in the majority of cases either to insufficient or indifferent supervision, or to the adoption of an unsuitable method.

The soaking of fresh market skins is comparatively simple. The only precautions to be taken are a full recognition of the necessity of a complete removal of blood and dung, and also salt, if this has been used by the butcher or hide salesman as a temporary preservative in warm weather. Blood, if allowed to go forward on the goods into the lime, is likely to cause stains on the finished leather, in addition to increasing the bacterial activity of the limes to an undesirable degree, by providing a suitable medium for the cultivation of bacteria.

Dung and dirt should be removed as carefully as is possible at this stage of the proceedings, as these also, but to a greater degree, contaminate the lime liquors with bacteria which militate against the plumping of the goods, in addition to bringing about a liquefaction of skin substance and a consequent loss of weight and "substance" in the tanned leather.

The soaking should be effected as expeditiously and efficiently as possible. The process is best done by placing the goods in a latticed drum which should rotate at not more than five to six revolutions per minute, and should be provided with a plentiful supply of clean running water; drumming the goods for about one hour, or until thoroughly cleansed, and then placing in a pit, with a clean fresh water soak, for a few hours before hauling and draining preparatory to passing forward into the lime yard.

Dung and other extraneous matters not effectively removed by the drumming, should be worked off over the beam, or a good method is to put the goods through the rubber roll putting-out machine; or in the case of wooled sheepskins, the burring machine.

Wet salted skins which have been treated with a plentiful supply of salt for the purpose of preserving the goods from liability of putrefaction when kept over a period if necessary of several months, require somewhat careful treatment in the soaking process, chiefly in the direction of insuring the elimination of the whole of the salt.

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Dry salted hides have been preserved by a thorough salting followed by drying with a view to lessening their weight and thereby economizing in freight charges; this class of goods being practically universally confined to imported stock, and also with the object of more effectively preserving the skins in order to enable them to be stored for a longer period, if necessary, than is desirable in the case of wet salted goods.

Salt acts as a preservative chiefly by reason of its effecting a partial dehydration of the pelt; the removal of the water from the skin limiting the liability of bacterial putrefaction. When dealing with this class of goods one essential of the soaking process is the restoration to the fibers of the moisture which has been removed by the salt treatment.

The second and perhaps more important result to be effected is the removal of the whole of the salt from the goods, before proceeding with the liming process. It has long been recognized that salt, in common with other chlorides, militates against obtaining the requisite plumpness in the liming process. Salt in strong solutions possesses a decided influence in the direction of solubilizing skin substance.

It will be obvious from what has been stated, that the soaking of salted goods should be effected as quickly as is consistent with the removal of the salt. The best method of carrying this into effect is to place the goods into a clean running water soak in a pit for two or three hours. The pit is preferably constructed with a latticed false bottom and provided with a plentiful water supply, which can be run in from the bottom of the receptacle, and overflow from the top, with a view to washing out the salt as quickly as possible.

The soaking can be done equally effectively in the case of wet salted goods in the latticed drum before mentioned. Dry goods are best soaked in the pit, as first described, and if necessary in order to complete the operation efficiently, subsequently drumming, followed by a few hours' soaking in clean water in the pit. Economy in the amount of clean water to be used is a false policy; the greater the amount of water used within reasonable limits, the more effective the operation. Salt, contrary to the ordinary public idea, is not a very soluble chemical, and requires a considerable quantity of water to dissolve it. Whereas, for

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example, 100 parts of water is only capable of dissolving 35 parts of salt, 197 parts of sugar would dissolve in the same quantity of water.

During cold weather the soaking can be facilitated by heating the soak water to a temperature of 75° F., but it is not to be recommended to soak at a temperature higher than this. The use of any but clean fresh water for each pack of goods is to be deprecated. Soaking is complete when the goods are quite pliable and soft, and free from salt. The latter can be ascertained by testing the soak water with a few drops of silver nitrate solution, when a white precipitate indicates the presence of salt. This test, on account of the fact that it is extremely delicate and reacts with a very dilute solution of salt, such as for instance a water slightly brackish, is therefore under these circumstances somewhat empirical in character, giving a positive reaction when only a trace of salt remains; but it is nevertheless useful, and with a little practice the practical man is able to judge of the approximate amount of salt remaining, by the amount of precipitation obtained by adding a definite quantity of the silver nitrate solution (say 5 drops of a 1 per cent. solution) to a test tube filled with the soak liquor.

The soaking of flint-dried skins is considerably more difficult to perform effectively than is the case when dealing with the goods previously mentioned. The method of drying adopted in eastern countries is always liable to produce difficulties for the tanner, on account of the gelatinous matter of the skin being often partially liquefied by the goods having been left exposed to the action of the tropical sun. When the skin has been heated to the temperature of boiling water it becomes practically insoluble. Whilst it is not suggested that this temperature is reached in the drying of skins for export in China, India and other eastern climates, the statement aptly illustrates the tendency towards insolubilization that is likely to occur when the temperature to which the skins are subjected is high. The gelatinous matter of the skin being partially gelatinized by the action of the heat, conduces in mild cases to cementing together of the skin fibers, and in extreme cases, of course, the deterioration of the fibers themselves ensues.

A further difficulty experienced in connection with dried goods

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of all kinds is that owing to the lack of care, particularly when the goods have been collected from country districts and have been dried by the agriculturalists in a very indifferent manner, putrefaction has taken place to a greater or lesser degree during the process of drying. If the putrefaction is present in only a mild form it is not possible to discern it in the dry imported skins, with any degree of certainty, and it is only when the goods are placed into soak that the damage becomes visible by the fact of the goods falling to pieces.

The problem to be solved by the practical tanner is how to get the goods back to their natural condition as quickly as possible and with as little loss of skin substance; also without putrefactive action.

The method of treatment of dry goods, notably East Indian kips and calf, most commonly adopted by the tanners specializing in the dressing of these goods some years ago, with a view to rapid soaking, was to place the goods into soak in a liquor which has been used over and over again for a considerable number of packs, in some extreme cases the soak liquor was preserved and used for years. A stale soak liquor of this description undoubtedly has a very considerable softening action upon the skins, but unfortunately from the point of the finished leather, whilst the soaking is rapidly effected, it is at the expense of a considerable amount of skin substance with the result that the goods when tanned are lacking both in substance and weight, and if immersed for a long period they are likely to be damaged by bacterial action.

This latter action was not generally understood, and the defects visible in the finished goods were commonly ascribed to putrefaction before the goods were put into soak. The putrid soak softened the goods quickly because of the presence of gelatine liquefying organisms and enzymes. These acted upon the partially dissolved gelatinous matter of the skin, which had been subsequently dried, liquefied it and thereby freed the fibers. If the goods were left in such a soak for a sufficiently short period, and the organisms were of the right kind, the soaking was effected with a minimum loss, but it will be obvious that if the goods were left for too long a period the solvent action of the gelatine-liquefying organisms and enzymes would not stop at the mere liquefac-

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tion of the gelatinous matter in which the fibers were imbedded, but would liquefy a considerable portion of the gelatinous matter of the fibers themselves.

The use of stale soaks has now been generally abandoned, except by one or two of the older-fashioned and more conservative tanners, and the use of this dangerous method has been replaced by the use of certain chemical salts.

The method of facilitating the soaking process by mechanical means which was very largely employed some years ago, particularly upon East Indian kips, was the operation of stocking. This process consisted of placing the goods into the stocks and sufficiently softening them by the stocking process for an hour or so. The process in question has now been generally abandoned by the more important tanners because of the considerable danger of breaking the grain of the goods in the event of their having been insufficiently soaked before subjecting them to the stocking, and the severe action of the process being liable to effect a loss of skin substance.

The common methods of softening by mechanical means are drumming and breaking.

The drumming is best done in either an open ended pin drum, or a latticed drum. The operation is one which requires care and a considerable amount of supervision of the goods before resorting to this process. If the goods are insufficiently soaked there is considerable liability of damage, and in any event the drumming operation should not be too prolonged. It is also important if the operation is carried out in a closed drum, that the goods should not be allowed to "heat," by too long continuous drumming, without ventilating the drum. It is generally considered advisable to drum for about 10 minutes and then stop for 10 or 15 minutes, before continuing. A peg drum is more effective for the purpose than a shelved drum, but here again care must be taken to see that the goods are sufficiently soft and flaccid, to prevent any liability of grain damage, before subjecting them to this somewhat severe treatment.

In the case of wooled skins the soaking is facilitated by either breaking by hand or on the burring machine, or else by the above mentioned drumming process. Breaking by hand over a beam with a blunt unhairing knife has a very considerable softening

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action, and the stretching of the skins by working upon them on the flesh side with the knife helps to free the fibers and soften the goods. In any event this is more effective than by passing the goods through the burring machine. The writer has seen a rubber roll putting-out machine employed also for this purpose with considerable effect, and though the results were not quite so good as by hand breaking, they were superior to the result obtained by drumming.

### Chemical Assistance in Soaking.

The number of chemical salts which can be utilized in the process of soaking is large, and they all depend upon the one action for their utility, *viz.*, the swelling of the fibers by either acid or alkaline agents, such swelling action having the effect, when used in conjunction with mechanical methods, of freeing the fibers from their embedded condition. Weak organic acids are very largely employed for this purpose, butyric, lactic, and acetic all having been used successfully; also inorganic acids, sulphuric, sulphurous and hydrochloric having been tried for the purpose.

A common method, and one which gives good results, is to place the goods into soak in clean water for 24 to 48 hours, until somewhat softened, and then transfer them to a fresh soak to which has been added a suitable quantity of one or other of the acids mentioned above. It is difficult to prescribe any definite amount of any of the acids to be employed, as the amount to be used depends upon the temporary hardness of the water used, the strength of the acid employed, and the degree of swelling desirable for the particular classes of goods in work. It may be stated, however, that the smallest possible amount should be employed. One pint of formic acid (40 per cent.) in a pit of 1,000 gallons water capacity, being usually sufficient to produce the required degree of swelling.

The goods should be soaked for 24 hours in a weak acid solution, or until slightly swollen and sufficiently soft to allow of their being bent over without springing back. When this has been effected the goods may then be carefully drummed with a view to facilitating the softening action still further. It is of course very important that the drumming should not be attempted until the

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goods are sufficiently soft, so as to prevent any liability of breaking or cracking the grain. When sufficiently soft the goods are drummed for about one hour, this being best carried out in a latticed drum without liquor. When drummed the goods may be placed back into a fresh soak slightly acidified with about the same amount of acid as the original liquor. Successive treatments of this kind are given until the goods are sufficiently soft and flaccid.

Alkaline soaking agents are employed to a very much greater extent than is the case with acids, and generally speaking the method is safer and quite as economical. The soaking agents most commonly employed are caustic soda or potash, sodium sulphide and ammonium carbonate. Caustic soda and potash exert a very rapid swelling action even if only an extremely dilute solution is employed. Sodium sulphide depends for its action also upon the fact that when it is dissolved in water the dissociation of the salt results in the production of caustic soda and sodium sulphide, the former being the swelling agent.

The aforementioned are extremely suitable when dealing with hides, calfskins and goatskins, but are unsuitable for use upon wooled skins, on account of the fact that the wool is injured by the action of the caustic alkalies. The swelling action exerted by the caustic alkali is similar to that obtained when the goods go forward into lime. It is not, however, desirable to abnormally swell the goods at this stage, a sufficient degree of swelling to effect the setting free of the fibers by the mechanical action of drumming or breaking above referred to, being all that is necessary. As in the case of acids, it is difficult to specify any particular amount, but a solution of about 0.1 per cent. of caustic soda, or slightly stronger (0.15 per cent.) sodium sulphide is approaching the maximum quantity desirable to use.

Ammonium carbonate is more expensive than the above mentioned, although, unlike caustic soda, it is allowable in weak solution in the soaking of wool skins. Apart from the fact that it is somewhat expensive, it has an influence upon the weight of the wool, by the saponifying action of the salt upon the natural grease in the wool, thereby reducing the yield in weight of the wool removed in the fellmongering process, and possesses the further liability of bringing about a form of lime blasting, when

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used in quantity, calcium carbonate being produced when the goods go forward into lime.

Several acid salts are particularly useful in the soaking process. Potassium or sodium bisulphite are cheap and efficacious, and have the further merit, particularly in the case of the bisulphites, that they may be used in comparatively large quantities without the liability of any damage. These salts of a weakly acid character possess sufficient swelling properties when employed as soaking agents to bring about the necessary freeing of the fibers, without liability—as in the case of the employment of acids—of abnormal swelling, which if carried to the extreme will bring about the actual bursting of the fibers themselves with consequent deterioration of the tensile strength of the finished leather. A suitable strength of solution to be employed in the case of flint dry hides or goatskins is from 0.1 to 0.2 per cent., and where the goods have not been very highly dried the strength may be reduced below the latter figure.

The bisulphite salt can also be employed in the soaking of sheepskins with considerable advantage, and in addition to facilitating the soaking of dry and dry-salted goods, *e. g.*, Cape, Australian and Arabian skins, it has the further advantage that without diminishing the weight and yield of wool, being a bleaching agent even if only a weak solution is employed, it has the effect of conducing to the production of a clean wool of a whiter color.

Bisulphates, which are cheaper than bisulphites, whilst bringing about an equal degree of softening, should be used more sparingly, and the goods should be preferably given a rinse through water before liming, with a view to freeing them from any excess which would be liable to bring about the production of calcium sulphate when the goods go forward into lime, the latter being insoluble and liable to bring about a somewhat similar defect in the finished goods to lime blast.

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## THE DETERIORATION OF LEATHER USED IN GAS METERS.*

*By M. C. Lamb.*

In the early part of 1913 the author was consulted by the South Metropolitan Gas Company, and at their request commenced a somewhat elaborate and lengthy investigation with the view to elucidate the cause or causes which were responsible for the rapid deterioration of the leather employed in the construction of gas meters.

The author now places on record the results of this investigation, so far as it has progressed, as a contribution to the general discussion on the important subject of "The Life of Gas Meters"; a preliminary report of a Joint Committee appointed by the Institution of Gas Engineers and the Society of British Gas Industries has recently been published (see *J. S. C. I.*, 1916, 824).

As is well known to gas engineers there has, of recent years, been a gradually increasing tendency on the part of gas meters to require repairing on account of either partial or complete breakdown of the mechanism of the diaphragm used as a measuring instrument for the amount of gas passing, thus interfering with the correct recording of the quantity of gas consumed.

The major portion of the complaints received were apparently traceable to the leather used, either in the form of a complete diaphragm, or perhaps more generally used to form the connecting bellows of two diaphragms made of tin plate, the leather having apparently undergone some form of deterioration, thereby losing its necessary property of providing a gas-tight medium.

*Meter Leather Requirements.*—The hitherto recognized requirements of the meter manufacturer, as understood by those three or four firms of leather manufacturers specializing in the manufacture of "meter leathers," may be summarized as follows:

(1) The leather, with one exception, that general usage has demanded has been the so-called "Persian" sheepskin, a native-tanned East India sheepskin. The selection of this particular class of skin was no doubt due to the fact that this leather, on account of its close texture and compact fiber structure, was less liable to porosity, and hence was considered more suitable for

* *J. S. C. I.*, Vol. 35, p. 989, Oct. 16, 1916.

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the purpose than domestic sheepskins, which possess a more open texture and porous character, and are naturally greasy.

(2) The leather, when dressed, must be supple, be free from excessive natural fat, and free from stretch; it is a necessary stipulation that the skins should be specially selected for freedom from holes.

(3) The substance of the leather is to a great extent determined by the size of the diaphragm upon which it is intended to be used—thin substance skins, *e. g.*, 0.4 to 0.5 mm. for 5-light meters, to from 1.0 to 1.5 mm. for the larger sizes.

(4) In the majority of cases the meter manufacturer stipulates that the grain of the leather should be removed by buffing, the object of this apparently being to make it softer and to increase its power of absorbing the oil and graphite mixture used as a finishing dressing; the buffing produces a surface which is capable of retaining a greater proportion of the dressing than is the case when the grain has not been so removed.

(5) The exception mentioned above (1), so far as the author is aware, only refers to one particular meter manufacturer in Great Britain, and is therefore in the nature of an individual experiment. The leather used is a split sheepskin of British tannage, known as a skiver, *i. e.*, the grain side of a sheepskin; it is of thin substance, has little tensile strength, and is liable, unless extreme care is taken in the selection, to be entirely unsuitable on account of its tendency to possess natural perforations known as "pinholes," due to the natural growth of the skin. It has been stated to be satisfactory in use, but in the author's opinion it is not suitable for general adoption on account of its somewhat irregular physical character and its low tensile strength, though the latter factor does not play so important a part as one might anticipate without a full knowledge of the internal working of the meter leather when in use, and its method of attachment. The fact of its employment is interesting, however, as showing that, with the one exception, every British meter manufacturer has adhered to the use of the East India sheepskin, and though this was not considered satisfactory, particularly during recent years, apparently no other kind of leather has been tested with the object of finding a better substitute, or the experiments have resulted in failure.

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*General Investigation of Causes of Deterioration.*—The investigations of the author were in the first place directed to the leathers employed and their condition after being in use for varying periods, as ascertained by examining the leather and diaphragms removed from a very considerable number of meters of many makes, returned to the repair shop of the South Metropolitan Gas Company.

This examination revealed the fact that in almost every instance the perforation of the meter leather was in a line drawn parallel to the periphery of the metallic diaphragm to which the leather was attached, the extent of the perforation varying from ¼ inch to, in a great many cases, 5 or 6 inches. The leather, on examination after having been freed from the remains of the graphite and oil dressing, whilst being sound and unaffected in the center of the leather strip, was hard and perished where it had come in direct contact with either the metallic band fastening the leather to the diaphragm, or with the diaphragm itself. In every case examined, the leather where it had perished and become hard was also discolored, and was in the majority of cases practically black. In one or two instances a narrow strip of leather had been placed in direct contact with the metal diaphragm, and under the meter leather, to act as a cushion when the meter leather was fixed by hemp cord or string; this strip of leather, which was protected from direct contact with the gas, had, in every case examined, become completely perished.

Subsequent analytical investigations showed that at the points mentioned the deterioration of the leather had undoubtedly been caused by iron, which had converted the tannin into a tannate of iron; this, by continuous oxidation and reduction, made the leather hard and caused it to disintegrate and perish. The amount of iron found was in some examples as great as 0.3 per cent. (Fe).

*Methods of Attachment of Diaphragms.*—Attention was next paid to the various methods of attaching the leather to the diaphragms as adopted by the various makers. These consisted of either (*a*) attachment by means of steel bands, most commonly covered to protect the band, either with linen tape or leather, or (*b*) attachment with several coils of hemp cord drawn tightly round the edge of the metal diaphragm, a cushion being made of

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a thin strip of leather as stated above, to produce a tight joint.

In the few cases examined where the metal band was covered with leather, it was found that the leather in contact with the metal band had also entirely perished and become black and brittle.

The author ascertained that some manufacturers, with a view to the production of a tight joint, used various adhesives to embed the leather when the band was tightened up, so as to close up and make gas-tight any small crevices or openings that might otherwise result. A number of these were examined, *e. g.*, flour paste, mixtures of resin and tallow, paraffine wax and tallow, and buck tallow. A sample of flour paste examined was found to contain an appreciable percentage of alum. Such a mixture must be unhesitatingly condemned, as owing to the free sulphuric acid liberated it dissolves the metallic band and thereby hastens the deterioration of the leather by transference of the resulting iron salt to the leather.

A mixture of ordinary tallow having, as is usual, a high "acid value," due to the condition of rancidity, must also be condemned for the purpose. Mixtures containing resin are also unsuitable.

The most suitable materials for the purpose, in the opinion of the author, if it is considered necessary to embed the leather in this way, are either paraffine wax, rendered sufficiently plastic by mixing with a small quantity of vaseline, or pure buck tallow, which must not possess a high acid value.

One of the earliest changes made in the repair shop of the South Metropolitan Gas Co., and which has since been retained after some three years' experience, was the substitution of an aluminium band for the steel band attachment. The employment of an embedding agent has been discontinued, as being unnecessary when the fitting was carefully performed.

It is of the utmost importance that the leather should be quite dry before it is fixed to the meter, and the stock of leather should be stored in a dry atmosphere; otherwise the moisture in the leather will quickly cause pitting of the tinned surface of the metal diaphragm at the points of contact with the leather, with consequent exposure of the iron surface.

*Oil Used in Dressing.*—Samples of the oil used by the meter manufacturers for mixing with graphite to produce a leather

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dressing were examined. Almond oil has long been employed for this purpose and has peculiarly suitable properties.

The oil used for the manufacture of the dressing should be a non-volatile, non-drying oil, and must remain liquid at low temperatures; it must also be an oil which does not become rancid and has a low "acid value."

Almond oil possesses all these properties. Other suitable oils fulfilling the necessary qualifications are peach kernel oil and apricot kernel oil; these are often used to adulterate almond oil, being cheaper, but for the purpose under review they are just as suitable.

Sulphonated oils are quite unsuitable either for use in the making of the graphite dressing or in the treatment of the leather.

It has been stated that manufacturers of meters in the United States do not employ any oil dressing in the leathers used. The advantage of the dressing as a protective covering against any injurious chemical impurities of the gas is obvious if reasonable care is taken that the oil used is the most suitable obtainable. The graphite acts as a filling agent, closing up the interstices of the fibers, and tends to produce a more perfect gas-tight medium. The use of petroleum jelly (vaseline) to replace almond oil has not been adopted, but it appears to the author to possess advantages that render it particularly suitable.

*Experiments With Meter Liquids.*—Several samples of the liquid condensate from a number of gas meters were examined. A number of samples were found to contain small amounts of ammonia and ammonium salts, compounds of cyanogen, and a fairly high percentage of inorganic non-volatile salts was found, and salts of iron and tin were present in comparatively large amounts. To ascertain the effect of the condensates on meter leathers, samples of different leathers were immersed in samples of liquids removed from meters in which the original leathers had been adversely affected. The results obtained were of a negative character; in every case the condensate had no appreciable effect when used as above, though the experiments were prolonged over six months.

An interesting experiment, which threw some light on the causes of deterioration, consisted of binding strips of leather round pieces of the metallic band used for attaching the meter

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leather to the diaphragm, and immersing these in meter liquids. The leather in every case, whether the steel band was protected or not with linen strips, deteriorated and was rendered brittle; the deterioration at those parts in contact with the metal was most pronounced, but also extended but to a lesser degree to those portions which were not in direct contact.

This experiment confirms to an appreciable extent the deduction formed on examination of a large number of leathers that had been removed from meters and which had probably perished, as mentioned above, owing to the corrosive action of the acid and ammonia constituents of the gas on the metal band.

*New Leathers for Gas Meters.*—Experiments were made with several leathers of different tannage from those ordinarily employed as mentioned above. Leathers of vegetable tannage are particularly susceptible to deterioration by the action of acid fumes and of alkaline gases; leathers tanned with mineral tannage agents are not so injuriously affected. In the light of this fact meter leathers were prepared of chrome tannage, also alum tannage, and semi-chrome tannage, which latter consisted of a vegetable-tanned East India (Persian) sheepskin from which the greater portion of the original vegetable tannage had been removed by treatment with weak alkaline salts, and replaced by retanning with basic chromium sulphate or chloride.

Leathers of these three different tannages were placed in meters, and to obtain a result as quickly as possible several meters were fixed in various parts of the South Metropolitan Gas Works where they were continuously in service; some few meters fitted with the experimental leathers were also placed on the ordinary circuit. At varying periods some of the meters were disconnected and the contents examined.

*Alum-Tanned Leather.*—The alum-tanned leather underwent considerable deterioration, and after a short period became hard and possessed the appearance of being undertanned, probably owing to the action of the ammoniacal gases. Previous experiments, made by immersing the leather for a lengthy period in meter liquids, had indicated the unsuitability of the leather, the meter liquid being found to possess a solvent action upon the tannage.

*Chrome-Tanned Leather.*—On the other hand it was found

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that the sample of chrome-tanned leather was quite unaffected, remaining soft and supple and apparently in as good a condition as when first enclosed in the meter.

*Semi-chrome Leather.*—The behavior of a well-chromed semi-chrome leather, so far as could be ascertained by the somewhat severe tests to which the samples of leather were subjected, was as encouraging as the fully chrome-tanned leather. Samples removed from the test meters after two years' trial showed no signs of deterioration whatever.

Samples of both the chrome and semi-chrome leathers were analyzed before and after the experiment. The results of the chemical tests showed practically no change in the leather, as given below:

| | Chrome leather | | Semi-chrome leather | |
|---|---|---|---|---|
| | Before Per cent. | After Per cent. | Before Per cent. | After Per cent. |
| Mineral ash..... | 5.7 | 5.9 | 3.25 | 3.3 |
| Chromic oxide .... | 3.0 | 3.0 | 2.1 | 2.15 |

The following tensile strength tests were made:

| Chrome leather | | Semi-chrome leather | |
|---|---|---|---|
| Mean of 4 tests of strips ¼ inch wide by 2 inches long. | | | |
| Before treatment | After | Before | After |
| 21.4 | 20.7 | 21.0 | 21.5 |

A careful comparative microscopical examination of sections of each of the leathers showed that the samples had undergone no deterioration of the leather fibers.

In view of the fact that the experiments had shown, so far as could be ascertained in the limited time over which the tests had been made, that the semi-chrome East India tanned leather was undoubtedly superior to the ordinary East India (Persian) in general use, it was decided to adopt this leather provisionally for general repair work and in the manufacture of meters constructed by the South Metropolitan Gas Company.

The following specification was eventually adopted with a view to obtaining from various contractors a leather that contained a sufficient chrome content to ensure that the leather had been properly retanned with the basic chromic salt, and having in view the most suitable treatment for the purpose of providing a leather that the experiments indicated to be the most promising.

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## Specification for the Supply of Leather Intended for Use in Gas Meters.

### *Semi-chrome East India ("Persian") Sheep.*

### *Material.*

1. The skins are to be dressed from a good quality East India tanned "Persian" sheepskin of naturally "dry" tannage.

2. The goods to be selected of as near as possible the requisite substance in the crust condition, in order to avoid the necessity of materially reducing the substance by shaving all over the skin.

3. The goods to be reasonably free from grain defects and "tick" and from flaying defects; the skins to be free from holes.

### *Dressing.*

1. The skins to be prepared by lightly stripping with borax, washing, and retanning with basic chromium sulphate or basic chromium chloride in sufficient quantity to give the required chromium content given below (2).

2. The leather to contain 2.0 per cent. to 2.5 per cent. of chromic oxide on the dry weight of finished leather.

3. The leather to be neutralized after retanning.

4. The fat-liquoring to be done with neats-foot oil and neutral soda soap, using an amount equivalent to 3 per cent. oil and 2 per cent. soap on the dry finished leather.

5. The leather to be staked, fluffed, and lightly buffed on the grain side, except when expressly stipulated that buffing is not to be done.

6. The goods to be soft full supple leather, and free from any inclination to hardness.

One of the advantages in favor of the adoption of this leather was that it could be supplied by any firm of leather dressers ordinarily engaged in the dressing and finishing of East India tannages.

Subsequent experience has inclined towards the adoption of real chrome leather made from a domestic or New Zealand lamb-skin, for use upon the smaller size meters, but retaining the semi-chrome tanned East India sheep for larger size meters. Real chrome leather in the majority of cases was found to be too soft and inclined to bagginess when employed upon large size meters, a defect which is conducive to incorrect registration. Semi-

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chrome East India sheep of 1 to 2 mm. thickness possesses, when properly dressed, the right amount of suppleness without any inclination to be so soft as to be liable to sag when used as the bellows of the meter.

The specification which has been provisionally adopted for real chrome lamb leather is as follows:

*Chrome Leather.*

*Material.*

1. The skins to be tanned from a domestic lamb skin or New Zealand pickled lamb pelt of good quality, of 6 to 8 square feet area.

2. The goods to be specially selected for freedom from cockle, and be reasonably free from butcher cuts, holes, and other defects.

3. The skins to be selected of as near as possible the required substance in order to avoid the necessity of shaving.

*Tannage and Dressing.*

1. The goods to be tanned by the chrome process, and to contain a minimum of 3 per cent. chromic oxide, calculated on the dry (degreased) finished leather.

2. The goods after tanning to be neutralized and afterwards fat-liquored with a minimum of 2 per cent. neats-foot oil and 1 per cent. soda soap on the dry finished leather weight.

3. No glycerine or other substance of a hygroscopic nature to be applied to the goods.

4. The goods to be staked, strained, and fluffed on the flesh side, and delivered in the original undyed blue color.

5. The skins to be supple, fully tanned, well nourished leather, and to be free from any tendency to hardness.

It is extremely satisfactory to report that since the adoption of the semi-chrome leather for use upon all meters of the South Metropolitan Gas Company, which change was made on the author's suggestion as far back as July, 1913, not one meter fitted with these leathers has been received by the repair shop for renewal of the leather, and in all the numerous cases which have been examined, including the original experiment and tests made on meters in continuous service, no deterioration of the leather has been observable.

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Whilst the author does not claim that the substitution of the two leathers above referred to is the final answer to the question under discussion, the practical result shows that the adoption is at any rate one step in the right direction.

The resistance of chrome leather (and of leather semi-chromed to such a degree that it possesses practically the whole of the essential properties of the full chrome product) to the action of small traces of acid, and of alkaline gases, was thoroughly investigated by the author some years ago,[1] in continuation of the investigations of the special Society of Arts Committee on the Deterioration of Leathers for Bookbinding, published in 1901.

It is also now a well known fact that the life of chrome-tanned belting leathers used for the transmission of power in chemical and other works, where they are subjected to various chemical gases, is much greater than is the case with ordinary vegetable-tanned leather, and also longer than is the case of the majority of cotton and other fiber belts.

In the recent report,[2] made by Dr. Lessing to the Joint Committee representing the Society of British Gas Industries and the Institution of Gas Engineers, reference has been made to the investigations of the Society of Arts Committee on the Deterioration of Bookbinding Leathers, referred to above.

Dr. Lessing gives details of analyses of 21 samples of leathers used for diaphragms in which the percentage of acid (in terms of sulphuric acid) varied from 0.54 per cent. to 1.37 per cent. in leathers that had not been used. These results are entirely contradictory to the author's experience.

As above referred to, the ordinary meter leathers are made from sheepskins tanned in East India, chiefly by native tanners in a comparatively small way of business. The term "Persian" applied to these goods does not indicate the source of origin, and is only a trade description that originated many years ago, when an importer having discovered these goods in India was desirous of eliminating competition for their purchase, and in order to mislead his trade rivals called them Persian sheepskins, which resulted in keeping the source of supply secret for some

[1] *J. S. Dyers and Col.*, 1908, 24, 160; *J. S. C. I.*, 1908, 820.
[2] See *J. S. C. I.*, 1916, 824.

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time; the original route for East Indian shipping was by way of the Persian Gulf.

No mineral acid is used by the native tanner in the manufacture of these goods, and in a lengthy experience of these goods the author has not known a single case where the leather has been found to contain sulphuric or other mineral acid in the original condition as imported.

The author can also vouch for the fact that the three principal leather manufacturers specializing in the manufacture of leather for meter diaphragms do not use sulphuric acid in the dressing of these particular goods. The use of sulphuric acid for clearing and improving the ground color of East Indian and other tannages preparatory to dyeing bright and fancy shades of color, was quite common before the investigation of the Society of Arts Committee, and resulted in the rapid deterioration of these leathers when used for bookbinding; this practice has now ceased upon these leathers, following the report in question. It has never been common in the case of meter leathers.

With reference to the statement made in Dr. Lessing's report that the presence of decomposition products of leather was found in the non-volatile residues obtained from meter liquids, from which he infers that there has been solvent action of the gas and meter liquids upon the leather diaphragm, the author would point out that some small amount of leather substance is invariably present in all meter liquids. This does not necessarily originate by reason of any solvent action of the gases or the meter liquid, but is often due to the fact that the leather on account of its having been subjected to mechanical attrition on both sides on an emery wheel, has a fine velvety nap surface, and if not carefully brushed before being cut up, introduces a quantity of leather dust into the meter which subsequently finds its way into the meter liquid. The samples of meter liquids examined by the author have had, as above stated, little solvent action upon pieces of leather that have been immersed in them for long periods.

The above results of the investigation are not considered by the author to be final, but, as stated in the opening paragraph, to be a contribution to the discussion on the subject. Further experimental work is in progress, and the author hopes to be able

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to communicate any interesting results dealing with this important industrial problem, in due course.

The author desires to take this opportunity of expressing his thanks to the Chairman of the South Metropolitan Gas Company (Dr. Carpenter) for granting him permission to publish the results of his investigations.

LEATHERSELLERS' TECHNICAL COLLEGE,
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London, S. E.

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## REGULATIONS FOR THE PREVENTION OF ANTHRAX.*

*Adopted by the Massachusetts State Board of Labor and Industries and published by them in pamphlet form.*

*By Thomas F. Harrington, M. D.*

The number of cases of human anthrax has increased greatly in this state during the past year. This disease is dangerous to the health and life of workers engaged in those lines of industry in which animal products are a part of the manufacturing process.

The State Board of Labor and Industries asks your co-operation in lessening, so far as is practicable in your establishment, the conditions liable to spread this disease.

You are requested to inform this Board of any means that you have taken or propose to take for the protection of the work people in your employment against anthrax. The Board will appreciate greatly any observations or suggestions bearing upon this subject that you care to offer for the information of this department and of other manufacturers.

The State Board of Labor and Industries presents the following as the basis for rules and regulations for the prevention of anthrax. You are urged to apply these suggestions in your establishment in so far as they are applicable to your special line of industry.

### PREAMBLE.

Anthrax may be transmitted to man by infected hides, skins, wool, horse hair, cow hair, goat hair, pigs' bristles or pig's wool, as well as by dried blood, bones and other animal products. The

* Reprinted in full in *S. & L. Rep.*, Oct. 19, 1916.

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bacillus of anthrax soon dies out when dried at the ordinary temperature, but the spores of the disease may remain active, under favorable circumstances, for many years. These spores, enclosed in blood clots, dried and caked on the hair, skin or wool, are the usual sources of infection, owing to the clots breaking up into dust. The dust arising in the handling, sorting and manipulating of the animal products readily finds its way into the lungs in breathing, or is swallowed in the act of eating or drinking. More often, however, the dust finds its way into broken skin by cuts, bruises or scratched pimples. The result of this infection is anthrax. Anthrax therefore is chiefly a dust disease. (It can be caused by eating diseased meat and by the bite of an insect which has fed upon infected carcasses or other material.) While the danger of anthrax is greatest, according to all statistics, in the manipulation of animal products imported from China, Russia and Siberia, nevertheless the disease is so widely distributed that in no country is it unknown. Consequently, the precautions which are most necessary where hides, skins, hair and wool from the countries named are handled can, with advantage, be applied to products from other countries. In the United States there is no interstate quarantine law nor disinfection regulation against anthrax.

Protection against anthrax can be grouped under these headings, *viz:*

1. Disinfection of the material.
2. Avoidance of dust.
3. The instruction of the workers.

The experiences of countries where anthrax has been more prevalent than it has been in this country shows (1) that wool or hair can be readily disinfected by steam without injury to the material, and (2) that hides and skins can be disinfected without damage to these articles and without injury to subsequent manufacturing processes.

The following rules and regulations shall apply to all establishments where hides, skins, fur, horse hair, bristles, wool, horns, bones or other animal products liable to be infected with anthrax are handled.

For the enforcement of these rules and regulations all products

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or parts of animals shall be considered in a raw state unless they have undergone a treatment as follows:

Hides and skins: tanning.

Wool: scouring.

Horse hair, fur and hog bristles: bleaching.

Horns and bone: boiling for two hours, or treatment with a strong antiseptic.

The following industries shall be considered dangerous within these rules and regulations, and they shall apply in a special manner in those departments where these processes are carried on, *viz:*

1. The unpacking, unloading or other handling, when dry, or before disinfection of the material.
2. The preparation of horse hair.
3. Tawing, tanning and fur dressing.
4. The pulling, scouring and sorting of wool.

## Disinfection.

All foreign[1] hides, skins, horse hair, cow hair or goat hair, pigs' bristles and pigs' wool, before they are manipulated in any factory or establishment in this state, shall be disinfected (unless exempted as hereinafter provided) at the choice of the manufacturer in one of the following prescribed ways:

### A. Hides and Skins.

(1) By the Seymour-Jones method, *viz.:* To 1 pound of perchloride of mercury add 500 gallons of water, and to this mixture add 5 gallons of formic acid (commercial 50 per cent. strength). In this bath steep the material for 24 hours; or,

(2) By the Schattenfroh method, *viz.:* In a 2 per cent. hydrochloric acid solution to which 10 per cent. of common salt has been added steep the material for a few days. A quicker method can be used by substituting a 1 per cent. solution of hydrochloric acid and 8 per cent. of salt, provided the temperature of the solution is maintained at 40° C. (104° F.) for a period of 6 hours.

### B. Hair, Bristles and Pigs' Wool.

(1) By letting a current of steam act on the material for not

[1] Also domestic whenever anthrax is prevalent in the locality from which the material has been obtained.

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less than one-half hour at a pressure of 17 pounds (0.15 above atmospheric pressure); or,

(2) By boiling for at least one-quarter of an hour in a solution containing 2 per cent. of permanganate of potassium, and subsequent bleaching with a 3 or 4 per cent. solution of sulphurous acid; or,

(3) By boiling in water for not less than 2 hours.

### Exemptions.

The disinfection by the manufacturer may be dispensed with if he presents proof in writing stating that the material has been disinfected in accordance with the requirements of the United States Treasury Department or of the Massachusetts State Department of Health.

The manufacturer shall not be required to disinfect white bristles which he subjects to a subsequent bleaching process before further manipulation, or which he has bought already bleached (so-called French bristles) and which have been kept apart from non-disinfected material.

Exemption from the requirements of Section B may be authorized by the State Board of Labor and Industries for those materials that, according to present experience, would be seriously damaged, or for those materials that can be certified to as having already undergone an equally effective disinfection in the country or State from which they have been exported.

Prior to disinfection prescribed by these rules and regulations only such steps as are indispensable to the examination of the quality of the material, to the prevention of their being spoiled, and to the preparation and the execution of the disinfection are permitted in relation to material required to be disinfected, *e. g.*, unpacking and preparing for disinfection.

The stock of non-disinfected materials which are required to be disinfected, or which are exempted from disinfection, shall be stored in separate rooms and kept apart from the stock that has been disinfected. Access to this room should be restricted as much as possible so as to avoid unnecessary exposure of workmen.

### Records.

The employer shall keep a record of the skins, hides, hair,

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bristles, wool and other material mentioned in these rules and regulations, in such a manner that the quantity, the source of supply, and, so far as is known, the origin of the merchandise received, as well as the time and the method of disinfection, or the reason for its omission, are clearly set forth. Such records shall be accessible to the State Board of Labor and Industries or its representatives.

SANITATION OF WORKSHOPS.

*Floors.*—In those parts of the establishment where material capable of transmitting anthrax is stored or manufactured the floors shall have a waterproof covering or other suitable material that permits the ready washing of such floors. The floors of these departments should be washed daily if the workroom is dusty or if cases of anthrax have occurred recently at the establishment.

*Walls and Ceiling.*—The walls and ceiling of such workshop or room, unless covered with a smooth washable coating or oil painting, should be washed frequently with a disinfectant solution. If whitewash is used this coating should be renewed on the outbreak of cases of anthrax among workmen employed in that establishment.

*Tables, Workbenches and Seats.*—These articles should be washed twice a week with a disinfectant solution—especially if cases of anthrax have occurred recently in the establishment.

*Ventilation.*—The workroom shall be well aired twice daily by means of open windows, for at least half an hour, *viz.*, during noonday meal hour and after the day's work has been finished, or before it has begun again. No workman should be permitted to remain in the room during this period.

*Dust Removal.*—In all workrooms in which dust is a factor there shall be an adequate exhaust system installed capable of removing the dust at its origin and conveying it to a suitable receptacle for subsequent destruction.

It is recommended that hides and skins be submitted to the ordinary "wet salting" processes immediately after flaying; or if cured by drying, that the hides and skins be converted back to the "wet salted" state by the formic-mercury processes as soon as possible.

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In horse-hair factories and horse-hair dressing, the sorting and heckling shall not be done except in special workrooms separate from the other workroom. The dust created shall be collected and destroyed.

Carding and dust extracting machinery, as well as mixing, willowing and heckling machines, shall be closed over and provided with an adequate and effective dust exhaust system. The dust shall be collected in a dust chamber and burned.

The treatment of wool, horse hair, hog bristles and furs shall take place whenever possible in closed vessels. In those operations, such as opening of bales or beating, which cannot take place in closed vessels the process shall be carried on in such a way as to allow the collecting of the refuse and its subsequent destruction.

### Personal Precautions.

Printed notices issued by the State Board of Labor and Industries shall be kept posted in a conspicuous place in each department setting forth the dangers of anthrax infection, the early signs and symptoms of the disease, and the precautions that shall be taken in order to avoid this infection.

Any employee who is suffering from a cut, scratch, pimple or crack of the skin that has not healed readily shall report the same to the person in charge or to factory physician.

Employers shall furnish to employees impermeable aprons and leggins (or rubber boots) in all operations where the body is liable to come in contact with the water used in tanning, scouring, boiling or bleaching of animal product.

Employees shall wear a suitable respirator (loose gauze cloth tied over nose and mouth may be used) while engaged in the dusty processes of handling, sorting or of manufacture.

Employers shall provide for the use of employees overalls and gloves when handling raw material and neck protectors when carrying raw material on the shoulder. Raw material shall be transported on carts or hand-barrows whenever practicable.

Employers shall see that the materials provided for the use of employees are worn by the persons for whom they are intended, and that when these articles are not in use they are kept in a special place, and that they are disinfected at least once a week.

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Dressing rooms, wash rooms and a suitable dining room shall be provided and fitted up outside the place where dangerous operations are carried on.

There shall be provided an adequate supply of running hot and cold water, toilets, washing and drinking facilities, all in accordance with the rules of the State Board of Labor and Industries on toilets. Lockers shall be provided so that street clothes and work clothes may be kept separate and apart.

Employees shall not bring food into the workroom. The eating of food in workroom shall be strictly prohibited.

Employees shall be required to take off their work clothes before entering the dining room, and to wash hands, arms, neck and face before taking their meals or leaving the premises.

Employers shall keep posted in a conspicuous place in each department a notice legible to all employees stating:

1. The text of these rules and regulations.

2. Workshop regulations imposing on employees the following obligations:

(*a*) To make use of the various working clothes and other articles provided for them by the employer.

(*b*) To make use of the dressing room and washing facilities.

(*c*) To take the necessary measures for cleanliness before eating and before leaving the workshop.

(*d*) To bring no food into the workroom.

3. The dangers of anthrax infection, and the precautions that should be taken to avoid them, and the necessity of employees reporting at once all skin affections.

4. Name and address of physician in charge of the medical service of the establishment.

NOTE.

The first symptom of anthrax is usually a small inflamed swelling like a pimple or boil. This is often painless. In a few days the pimple becomes black at the center and is surrounded by other "pimples." The poison is now liable to be absorbed into the system, and will cause risk of life if not removed by prompt and effective treatment. Early treatment is usually suc-

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cessful; delay or neglect usually leads to blood poisoning, often to death.

[In the *Shoe and Leather Reporter* of Oct: 19, following the Massachusetts Regulations for the Prevention of Anthrax, is a statement from C. R. Oberfell, President of the A. L. C. A. He calls attention to the fact that the Seymour-Jones method of disinfection is not efficient in all cases, as shown by Dr. F. W. Tilley. (See this JOURNAL, March, 1916, pages 131-60; see also the discussion in the July number, pages 339-60.) Further, he points out that experience has shown that the Schattenfroh method is not free from danger to the hides, affecting unfavorably the quality of the resulting leather.]

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## SOME SIMPLE CHEMICAL TESTS FOR LEATHER MAKERS.*

*By A. Harvey.*

It is now an established fact that a chemist is indispensable to a firm whose ambition it is to produce the best quality material at the lowest cost. From the point of view of the leather manufacturer, the word "adulterated" at once brings into his mind's eye a leather containing Epsom salt or glucose; but of the hundred and one materials used in the making of the various classes of leather, the majority are open to adulteration. As adulteration—through the aid of science, I regret to say—has been brought to a fine art, the question of detection is made all the more difficult. Below, however, are appended a few simple tests which may be applied to several of the more common materials used, without the aid of a specially fixed laboratory or any expensive apparatus.

(1) *Lime.*—A good quicklime should slake well when mixed with water. If, on the addition of a little hydrochloric acid (spirits of salt) it effervesces, it points to a fair amount of chalk present, while if after this treatment with acid much is left undissolved, it would indicate an excessive quantity of sand or insoluble matter.

(2) *Linseed Meal* (Crushed Linseed).—Make a solution in hot water, and allow to cool. When cold, add a few drops of tincture of iodine. A blue color formed would show that the linseed had been adulterated. (The blue color really indicates the presence of starch, and pure linseed contains no starch.)

* *Leather World*, Sept. 14 and Oct. 12, 1916.

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(3) *Dried Blood.*—If the amount of ash is determined, it should be between 4 and 5 per cent. It should be noted that the ash should be white. If of a brick-red color, the admixture of iron would be shown.

(4) *Gum Arabic.*—The likely adulterant is gum tragacanth. Dissolve some of the gum, after finely powdering, in the blue solution obtained by adding ammonia to a solution of bluestone (copper sulphate). If an appreciable amount is left undissolved, tragacanth is probably present.

(5) *Dyes.*—To determine whether a dye is just a simple one or an admixture, the following procedure should be adopted: Place a small portion of the dye on the end of a penknife, and blow it on to a piece of wet white blotting paper held about a foot away. The small particles will then adhere to the wet paper and dissolve in the water, showing its color. By this method one may show, for example, that a dye consists of a mixture of a blue and a red dye.

(6) *Cod Oil.*—This is likely to be adulterated with mineral oil. Boil up two or three drops of the oil with caustic soda which has been dissolved in methylated spirit. If after continued boiling a perceptible amount is left undissolved, this would indicate admixture with mineral oil.

This test is based upon the fact that, under the influence of caustic soda, cod oil is converted into soap, whereas mineral oils are not so changed.

(7) *Glucose.*—This substance may be adulterated and if a small piece is burnt in a tin, only a very small amount of a white ash is left. Anything over a trace would indicate adulterants.

(8) *Salt.*—Impure salt may contain a small yet undesirable amount of iron. To test for this, make a solution of the salt in water, and add to it a few drops of potassium thiocyanate. In the presence of iron, a red color will develop. If this chemical is not at hand, add a few drops of potassium ferrocyanide (yellow prussiate), when a blue color will indicate iron.

(9) *Ammonium Chloride* (*"Sal Ammoniac"*).—This should be of a pure white color, and perfectly soluble in cold water. If a small amount is heated in a tin lid over a gas flame it will be completely volatilized, no residue being left at all.

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(10) *Caustic Soda.*—This substance, if left exposed to the air, will absorb carbon dioxide therefrom, and so gradually "carbonate." A rough test would be to dissolve a little of the sample in cold water, and then add a little hydrochloric or sulphuric acid (dilute). If gas bubbles are given off, this would indicate carbonates, which in a good sample should not be present.

(11) *Ferrous Sulphate ("Green Vitriol").*—A good sample should be of a uniform pale green color. In a moist atmosphere it is liable to undergo oxidation, in which case a brownish color will develop. To prevent this, the material should be kept in a cool dry place, for preference in large stone jars fitted with bungs.

(12) *Sodium Thiosulphate ("Hypo").*—It is quite unlikely that this chemical will be adulterated, but as in appearance it resembles soda, it may be confused with this if, say, the labels became detached from the receptacles in which they were kept. Add a little hydrochloric acid to a solution of the substance in water. If hypo, the solution will turn yellow (owing to the fine precipitate of sulphur) and an unpleasant smelling gas will be evolved (sulphur dioxide). If, on the other hand, the substance be soda, only bubbles of an odorless gas will be given off (carbon dioxide).

(13) *Flour.*—Alum is sometimes added to a bad quality flour in order to improve its appearance. To test for this substance, the following reagent has to be prepared: 10 cc. of 5 per cent. alcoholic logwood solution mixed with 150 cc. of water, and 10 cc. of saturated ammonium carbonate solution. (This reagent should be mixed just before using.) Some of the flour to be tested is made into a paste with water, and then a few drops of the above solution added. Alum, if present, will be indicated by the formation of a blue color after the mixture has been allowed to stand for about two hours.

The percentage of ash also affords a good method of determining the quality of a flour. High-class flour yields 0.5 per cent. of ash, whereas lower qualities will give from 0.5 up to 8 per cent., according to how much "bran" is present. Chalk, which some years ago was used as an adulterant, can be tested for by adding dilute hydrochloric acid to some flour paste, when an effervescence will take place if chalk is present.

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(14) *Egg Yolk.*—It is difficult to suggest any simple tests for the purity of egg yolk, a chemical analysis being essential. The following tests, however, will detect the preservative present: Ignite some of the yolk to complete ash in a porcelain basin. If a large amount of a white ash is left, salt (sodium chloride) is the preserving agent. Now add to the ash a few drops of sulphuric acid, and then some methylated spirit. Warm the whole, and then ignite the spirit. In the presence of boric acid, a greenish tinge will appear around the edge of the flame.

(15) *Ammonia or ammonium hydrate* is a solution of pure ammonia gas in water, and at its greatest strength has a specific gravity of 0.880. A higher gravity than this would indicate either a weak liquor or the addition of water. If some of the solution is boiled to dryness in a dish, no residue should be left. Sulphates, chlorides, and other impurities are deposited by this treatment.

(16) *Borax.*—It is unlikely that this substance will appear adulterated, although soda has been stated to have been used for this purpose. This could be detected by treating some of the borax with some dilute hydrochloric acid, when, if soda is present, bubbles of gas will be evolved.

(17) *Mineral Acids.*—The two acids of this class used are hydrochloric and sulphuric, and to distinguish between these two, the following tests may be applied: Add to the acid (previously diluted with a little distilled water) a small quantity of silver nitrate solution. If a precipitate is formed, hydrochloric acid will be indicated. Using a fresh sample of the diluted acid, repeat the above experiment, using a solution of barium chloride in place of silver nitrate. A white precipitate will show sulphuric acid. By these tests, small amounts of impurities may be detected in either acid; for example, a very slight precipitate in the case of the first test will show a trace of chloride, etc. Iron may be detected in either acid by means of potassium sulphocyanide.

(18) *Shellac.*—The only impurity which can be demonstrated in a simple manner is any weighting material added, such as sand, etc., which may also be present in a dirty sample. Such substances will be left behind as insoluble residue when some of the material is dissolved in hot methylated spirit or hot ammonia

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solution. A good sample will dissolve completely in either of these two solvents.

(19) *Soda.—Washing soda or sodium carbonate* may contain iron and salt. Take some of the sample and dissolve it in some dilute sulphuric acid, or better still, some dilute nitric acid (aqua-fortis). Divide the solution into two parts, and to one add a few drops of silver-nitrate solution, when a white curdy precipitate will show the presence of salt. (If only a white cloudiness appears, a trace of salt is present.) To the other half of the solution add some potassium sulpho-cyanide, when a blood-red coloration will indicate iron.

(20) *Carbolic acid, or phenol,* which is sometimes used as an antiseptic, is liable to contain an undesirable amount of iron. The following method will apply: About half an ounce of the sample should be burnt to an ash in a porcelain dish. This operation should be performed in a place where the fumes evolved can be carried away—this is important. Then dissolve the ash in a few drops of strong nitric acid and dilute with a little water. The usual test for iron with potassium sulpho-cyanide may then be applied.

(21) *Sumac.*—The purity of this material, like all other tanning materials, can only be determined by an accurate chemical examination. Iron in a metallic form may sometimes be present in an undesirable amount. This may be tested for by running a strong magnet through a sample of the sumac previously spread out in a thin layer. The particles of iron will then adhere to the magnet, and may be removed and further examined if necessary.

(22) *Lactic Acid.*—If this acid has been adulterated with mineral matter, a large amount of residue will be left when some of the acid is boiled to dryness in a porcelain dish. To test for iron, the residue obtained above is dissolved in a little dilute nitric acid, diluted with a small quantity of water, and then a solution of potassium sulpho-cyanide added. If present, iron will give a deep red color.

*Note.*—This test also applies to acetic or formic acid.

(23) *Soaps.*—Soap, whether hard soap or soft soap, is very liable to adulteration with various admixtures. The sample should be cut into very small pieces, and a little of it boiled in absolute alcohol (or very good re-distilled methylated spirit may

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be used). Only soap will be dissolved by this treatment. What is left will be alkaline carbonate, borate, silicate, together with any "filling" material, such as starch, chalk, and, in very bad cases, even sawdust.

*Note.*—It might be added that to detect iron in any material containing a large amount of organic matter, the following method may always be applied: Burn the material to an ash in a porcelain (or better still a platinum) dish, and then heat the ash, when cool, with *nitric* acid. The addition of *this* acid is important, inasmuch as it converts all the iron present into the *ferric* condition, which is essential for the final test. Having now got the iron in solution in this form, the liquid is diluted with a little water, and then a little 10 per cent. potassium sulpho-cyanide solution is added, when a red color shows the presence of iron. If preferred, a 10 per cent. solution of potassium ferro-cyanide may be used instead of the sulpho-cyanide. In this case, however, a deep *blue* color will be produced if iron be present.

*Indicators.*—By means of indicators one is able to tell whether a liquid has an acid or alkaline reaction. The following table gives the colors produced when using these various indicators:

| Indicator | If Acid | If Alkaline |
|---|---|---|
| Litmus | Red | Blue |
| Methyl Orange | Red | Yellow |
| Phenolphthalein | Colorless | Red |

## DRUM-TANNED SOLE LEATHER.*

*By A. E. Langton.*

Amongst the uninitiated it is often assumed that tanners can produce sole leather in a few days by means of drum tanning. It may be granted that there are very few tanners who have not tried to do so, and reluctantly reverted to their old processes of pit tanning. The reason is that it was found to be almost impossible to get anything like the return of weight such as that obtainable by pit tannage, and the only recommendation was the time gained against the loss in weight. Now loss in weight from a normal return is a serious matter, and makes the leather come out at least 2d. to 3d. per pound dearer, even when there is no

* *Leather World*, Oct. 12, 1916.

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scouring to be done, as there is, of course, no bloom in a drum tannage.

It makes one wonder how it is that continental tanners favor drum tanning to such a large extent, but the reason may be that the return in weight was largely assisted by adulteration or "artificial weight," as they term it.

Now the process of drum tanning is a very exacting one, and needs a large amount of care to obtain any degree of success. The great secret lies in the ability to feed the pelt without getting it too hard to absorb the tan, and thereby closing up all the pores and making it case hardened. This means that very acid liquors must be employed in the early stages to keep the pelt open and plumped until it is struck through, and then to add the extract in increasing strengths until it is practically neat.

The best materials to use for this purpose in the early stages are myrobalan liquor or extract and quebracho, with the addition of plumping acid, and it is of the utmost importance to examine the goods at this period at least every three hours after running, to see that the goods are not getting pipey or flabby.

It is remarkable how quickly the pelt absorbs the tannin in the liquor, and if the drum is left to run when there is nothing but water left in it, the grain immediately gets loose. It is therefore of primary importance to keep adding stronger material to feed the pelt as quickly as possible after absorbing the former quantity given, and to keep it up by adding chestnut extract in increasing quantities and strengths as the tan penetrates the leather. This is perhaps the almost exact counterpart of pit tanning, but it needs more careful and accurate handling in a drum.

It is very necessary to estimate the weight of pelt in the drum to commence with, as it is the only method to gauge the amount of liquor required to cover the goods. It is not sufficient to put in 50 or 100 butts or shoulders as they rise, as the substance of pelt to be tanned is important, and to make any success, goods of the same or approximate substance should be classed together in parcels, otherwise some leather will be over-tanned and some under-tanned.

The liquors should not be heated in the early stages if a closed drum is used, as a certain amount of heat is generated in working. When the denser liquors are used, it is preferable to keep

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them warm, as the tanning process is thereby quickened. In an open drum it is difficult to keep any warmth, except for a very short period.

In some drums there are facilities for keeping the leather rigid whilst the drum is in motion, but this does not do away with the creasing of the grain, which it is supposed to obliterate.

The drum, however, is particularly useful for finishing bellies and shoulders, or tanning them right through if desired. Offal is always looser and more open than butts, and it is not difficult to get a fairly satisfactory leather from the process, though the leather is always more "grainy" than the pit-tanned product. Still, this is not so detrimental if the leather is solid and a fair color, and the difference in values is very small compared with the saving of time and cost of production. It is surprising what a good colored leather can be produced if the right materials are used, especially if the extract is well decolorized.

Judging from experience, the drum can most effectively be used for bends by first coloring off in the pit, and then filling the leather by drum tanning. The grain is more or less set, and the color also, and it is not difficult to keep the color and get the tan well into the leather. This is substantiated by the ease with which mellow light-tanned leather can be turned into good sole leather in a few hours in the drum, especially such goods as rough-dressing leather, Australian leather, or East India kips, though the latter have not enough in them to make a solid leather, though they will absorb plenty of tan. Still, in these times of stress and labor shortage, it is imperative to use every labor-saving device possible, and speed up every process that can be done without injury to the leather. Many sole leather tanners have realized this, and after coloring off their bends will dry them out, and then complete the tanning process in the drum. It saves time, and gives a fair return in weight, and there is no time for deterioration of liquors, as in the pit. It is also more economical, as it can generally be estimated how much material is required, and will be absorbed by the leather, and only this quantity is used. At the same time it is a surer guide as to the cost of tanning, though this can only be reckoned over periods to be a safe guide. There are some yards in the States where they employ men to book the labor on every batch of goods and

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the amount of tanning materials used, but no two lots of leather ever cost the same to produce. Therefore, except for tuning up at certain stages, there does not appear to be much gained, as compared with the system employed in this country.

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## CHAMOIS LEATHER MANUFACTURE.*

*By H. A. Winslow.*

The essentials of good chamois leather consist of extreme softness, a fine nap on one side, and non-resistance to being pulled into any desirable shape within certain limits. It is obtained in the first instance by splitting the already limed sheepskin by suitable machinery, into two portions, the flesh side, termed the "lining," forming the raw material for chamois, while the grain eventually becomes a skiver.

Before further treatment, the lining must be again put through the splitting machine to remove the thicker portion of the back—consisting of fat principally, combined with a small amount of skin tissue. Many dressers prefer to frize the linings instead of the second splitting, which operation is accomplished by throwing the skin over a beam and paring away the thicker portions and all unevenness with a suitable sharp knife. It is a form of fleshing operation, but requires practice and skill, as the skin is very thin and easily damaged.

The rejected portions of skin and fat are subjected to steam heat, and produce eventually gelatine or glue and tallow.

To obtain the necessary softness and flexibility, it is necessary to further lime the lining, which is done by placing the frized or second time split goods into lime pits, preferably an old lime, for a week, drawing alternate days. This will have the effect of further opening out the fibrous formation of the skin, but it should not be carried too far, otherwise the substance and strength of the resulting leather will be depreciated. Great precautions should be taken that the skins are not allowed to become dry in this stage, otherwise considerable loss will ensue.

After the second liming, the drawn and drained goods are passed through a bran drench to neutralize the lime. In yards

* *Leather World*, Oct. 12, 1916.

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where the tanning of skivers is carried on as well as chamois dressing, the bran drench, after being used for skivers, may be again used for the linings, and if not sufficiently acid to neutralize the lime present, an addition may be made of lactic, formic, or other similar acid in very small quantities. As an alternative, lactic acid of 1 per cent. of the weight of raw skin, added to luke-warm water sufficient to allow the goods to be easily moved about, may be used, and will be found to answer the purpose and accomplish all that is necessary in about one hour's time. A paddle should be used for this purpose to insure continuous movement of the skins during the period of treatment.

It is now necessary that all water should be expelled from the skin that may be possibly done without allowing any portion to become too dry. This is often done by placing the goods in a hydraulic press to squeeze out the excess of water. Originally hand wringing was the mode. Advantage is now, however, taken of the hydro-extractor or "whizzer," as used in woolen and cotton mills, and this method is found expeditious and very satisfactory, the excess of water being rapidly expelled without fear of the raw goods becoming too dry. When wrung by hand, or pressed, it was further necessary to treat the linings in the stocks with sawdust to absorb moisture, but with the extractor this may be avoided.

Having reached the required state of dryness, the goods now in the stocks are treated to successive quantities of cod oil while the milling action is proceeding. The quantity of oil given depends upon the amount of skin to be treated, as the latter should be saturated with oil, but not having free oil running away from them. After milling in the stocks, the goods are closely packed in bins or boxes and wrapped up. In a short time heat becomes noticeable, accompanied with the decided presence of a pungent smell which attacks the nostrils, causing a free flow of tears from the eyes of the workers handling the goods. The man in charge continually examines the goods, and when he finds the heat is high enough, he has the bins emptied quickly, and the contents spread over a floor space for cooling.

The color of the skins now begins to assume a dark brown. Examination must decide if sufficient oil has been used, and then the goods are again milled, to be again packed away in bins, fol-

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lowed by cooling. When the skins are approaching the dressed stage, they will be found to have a leathery feel, and to have lost the suggestion of raw pelt altogether. The tendency to heat in the bins gradually becomes weaker, until the skins may be hung up in a warm stove to finally exhaust all heating properties.

To remove the oil, steeping in warm water, and wringing out the goods repeatedly, is often done, the resulting liquid emulsion being known as degras. Another method is to form an emulsion of the nature of soap by submitting the goods to a solution of weak caustic potash in iron drums, and then pressing out the solution from the leather by mechanical means. The liquid so recovered is neutralized with sulphuric acid, and the freed oil becomes the sod oil of commerce.

Following the cleansing from excessive oil comes the drying of the leather, which is best accomplished by hanging it up in an airy loft. If, however, the leather is to be bleached, it is hung up in a drying room, so built as to prevent ingress of outside air. In the basement a quantity of sulphur is burned, while the door is closed from the outside. The action of the sulphur fumes upon the damp leather is to produce sulphurous acid, which considerably bleaches the skins, and gives them a uniform light color, while drying them at the same time. Several hours are needed to effect the bleaching thoroughly.

For some purposes—including dyeing—it is necessary to have white leather. This may be obtained by placing the damp leather in the sunlight, by laying out each skin upon the grass. This is a long process, depending upon atmospheric conditions, and is not much in use. A good white may be obtained by immersing the leather in a solution of permanganate of potash, until a good brown color results all over the skins. Horse up to drain, and then place in a bath of hyposulphite of soda and weak hydrochloric acid, or the latter bath may be made up of hydrogen peroxide solution, containing a small quantity of acid. In the latter case the sulphurous smell is absent, but the cost is a little more. Before using the solution of permanganate of potash, the leather should be freed from all soapiness and alkali by well washing.

When leather is bleached by this process, it must be repeatedly washed to remove traces of acid, so that it may receive a dressing

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of soap solution, in which a little oil is poured, say castor oil, to regain the softness and flexibility which the acid, if present, would remove.

After drying, the ordinary leather is damped, staked, and grounded. The best skins, being grounded on both sides, produce chamois, while thin or poorer selections are treated on the flesh side only, and are known as pockets.

Mechanical means are often substituted for hand labor in grounding skins, the principle being to grind the rough surface of the leather with an emery-covered wheel. In practice the wheel surface soon becomes clogged and smooth, which renders it ineffective for the purpose. If, however, the soapy solution or degras is all removed from the leather by well washing before drying, a wheel may afterwards be used with success. But to obtain the accustomed handling of the old-style chamois, the leather will have to be dressed afterwards with a fat-liquor, as described. When dry, the nap may be raised by revolving the goods a short time in a dry drum, pegged or shelved before laying them down.

Laying down constitutes the last stages of the process. Damped skins are separately laid upon a flat table, each shank under a weight, with additional weights at the butt, sides and neck, the operator stretching the skin in the required direction before placing upon it the weight. By this means the leather is fully extended to its utmost, while the required shape is obtained. The skins are laid one upon the other until the height is inconvenient for the worker, when a new pile is commenced. Cutting and sorting into sizes for sale completes the process.

Chamois may be dyed to any color required, and produces very beautiful results. Bleached by the permanganate process, dried, and grounded, they are wetted back, and are then ready for dyeing.

Perhaps the best results have been obtained by the use of the direct cotton colors, as these will work satisfactorily in the presence of soap, which is essential to retain the characteristic "feel" of chamois leather. Some alizarines have been used with satisfactory results, but a preference was shown for the colors before mentioned. The dyeing is accomplished in a drum or paddle as for other leather, and the skins are dyed quite through.

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Another method is to mix the color into a thick consistency with the aid of water and clay. For delicate colors, china clay may be used, while for dark ones, ordinary clay will do. This thick mixture is brushed into the surface of each skin, one at a time and allowed to dry. Afterwards the dry clay is beaten out of the skins. Of course, the color is not fast, and the more vigorous the beating, the paler the shade of color. But the leather is colored on one side only, which is necessary for some purposes.

For gloving work of the best description, the yolk of eggs is added to oil and a little soap, to produce a dressing which will give that excessive suppleness and fulness to the finest glove leather.

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## ABSTRACTS.

**Chemical Composition of Osage Orange Wood as Compared with Fustic.** From *Year Book of Agriculture* for 1915. A study of the extract obtained by leaching the ground wood or shavings of osage orange with water showed the dyeing principles present to be morin or moric acid, and moritannic acid or maclurin, the same as those in fustic, and a very small amount of a third, unknown red constituent. This red constituent is found in relatively large amounts in fustic from some localities, for example Mexico, and in comparatively small amounts in material grown in Jamaica and South America. Its practical absence from osage orange, however, is an advantage rather than a defect, since any considerable quantity of it tends to reduce the purity of the shades obtained and to give them a muddy or murky appearance.

[Extract made from osage orange, both in paste and powder form, is on the market under the name of "Aurantine."]

**Canaigre in Queensland.** *Leather Trades' Review*, Oct. 11, 1916. Canaigre is a tuberous-rooted plant much used in the past as a tanning material in Queensland. It goes also by the names of "red dock," "tanner's dock," and "wild rhubarb." It is propagated by planting the small tubers, and also by seed. About 1,000 pounds of tubers will plant 1 acre. It may be cultivated on arid soils, as it requires very little moisture. It cannot be injured either by heat, cold, wind, disease or insects, although, as regards cold, very heavy frosts are injurious to the plant. The best season for planting in Queensland is from April to May. The tubers are set in rows 2 feet apart, the plants in the row being 12 inches apart. The tubers rapidly increase in size, and form a cluster like sweet potatoes, growing very near the surface and sometimes on the top of the ground. The yield ranges from 6 to 10 tons of tubers per acre. When ripe they are sliced and rapidly dried. They contain up to 48 per cent.

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of tannic acid, the average being about 30 per cent. Two and one-half tons of dried roots will make 1 ton of extract, worth £12 to £14 per ton; 3 tons of fresh roots make 1 ton of dried. As a tanning material it is very valuable. For light leather it is stated to be superior to oak, gambier or hemlock. It is a quick tanner, and the yellow color absorbed by the hide in the process of tanning is considered highly desirable for certain leathers. The plant thrives in Queensland, and has been successfully grown at the State farms.

**Burmese Myrobalans as a Tanning Material.** *Indian (Government) Trade Journal,* Sept. 15, through *Commerce Reports.* A report on the Burmese myrobalans or "pangia" fruits as a tanning material, prepared by the chemical adviser to the Forest Research Institute, states that the Burmese myrobalans are different from the Indian Chebulic myrobalans in points of tannin and non-tannin contents and color. In the air-dried Burmese material the tannin varies from 16 to 32 per cent.; the general average may thus be taken to be 20-25 per cent., which is about half the tannin content of the Indian myrobalans. The non-tannin ranges from 25 to 34 per cent., and the general average may be taken to be 27-30 per cent., which is three times that of the Indian myrobalans. The color is high. The maximum red and yellow recorded for the Indian myrobalans is 2.5 red and 7.4 yellow, while the Burmese myrobalans in general have 4.9 red and 18.35 yellow. The excess of non-tannin is a disadvantage, and all tanning materials having non-tannins in excess must be classed as somewhat inferior, though in practice they give fairly good results. To form some opinion as to the actual tanning properties of the Burmese myrobalans experiments were undertaken, which disclosed that leather made with this material alone is spongy and tough like the leather produced by Indian myrobalans, that the Burmese fruits can be used in the preparation of butts for making army boots and shoes and also for making black uppers of inferior quality, and that they will be useful in conjunction with babul bark for making sole leather.

**Hides and Skins from Calcutta.** *Commerce Reports.* The hide and skin trade last year increased in quantity by 17 per cent. and in value by 20 per cent. In hides the expansion was 23 per cent. and the value 24 per cent., but in skins the increase was only 1 per cent. in quantity and 10 per cent. in value. Prices were higher throughout the year. Under hides the increase in shipments to the United States and Italy was large, the respective percentage increases in quantity being 64 and 416. The United States, deprived of its Russian source of supply, took increased quantities of buffalo and cow hides from every country that was in a position to export, which accounts for the marked increase in the total exports.

**Tanneries in French Indo-China.** CONSUL L. P. BRIGGS in *Commerce Reports.* There are in Tonkin nine tanneries, one at Hanoi owned by La Société des Tanneries de l'Indochine and eight small Chinese estab-

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lishments in Haifong and vicinity. The Chinese tanneries use 15,000 or 20,000 hides per year; the Hanoi tannery used 40,000 hides in 1915 against 30,000 the preceding year. The total value of the 1915 leather product was about $100,000. The increased output of the Hanoi tannery was due mainly to reorganization, but the low price of native hides, due to lack of tonnage for export, and the high price and difficulty of obtaining leather, due to the same cause, have given a hopeful stimulus to this industry. Machinery has already been purchased for a boot and shoe factory in connection with the Hanoi tannery.

**Switzerland's Demand for Leather.** CONSUL WALTER H. SCHULZ, Berne, in *Commerce Reports.* The needs of Switzerland in the leather trade are in the hands of an import syndicate, known as Importstelle des Verbandes Schweiz, Lederhändler, Laupenstrasse, Berne, Switzerland. Dr. W. Martin, of Berne, manager of the syndicate, declares himself ready to submit offers from American exporters to any member interested in the lines offered. A detailed offer, therefore, in quadruplicate for distribution and addressed to the syndicate should not fail of a hearing. The by-laws of the syndicate contain statements regarding the rules that govern imports. A similar syndicate, but not in this consular district, is the Import-Syndikat der Schweizerischen Schuhindustrie, Alten, Soleure, Switzerland. Its membership is composed principally of shoe operators of the country. It is believed that this syndicate also would welcome offers from the United States. The trade is especially anxious to obtain sole leather. Offers of hemlock, as well as split leather, therefore, should excite great interest. There is also a very large demand for light leathers, such as chamois, linings, sheep, etc. The big stocks of uppers, glazed kid, and patent leathers, in the country at the outbreak of the war, and big subsequent shipments account for the present small demand for that class of goods except for chevreau, which, it is believed, would find a ready sale. Germany, in former years, supplied the country with split leather obtained by it in the raw state from the United States.

**Tanning Industry at Madras.** *Commerce Reports.* The predominating article of export from Madras is leather. This consists almost entirely of cow and buffalo hides tanned, but not curried, and of goatskins and sheepskins tanned, but only partly dressed. From all the great seaports of India—Calcutta, Bombay, Madras, Karachi, and Rangoon—there is a considerable export trade in hides and skins, but it is only from Madras and Bombay—chiefly from the former—that these articles are sent out of the country in large quantities. The lightly tanned hides exported from Madras are retanned in foreign countries for conversion into "upper leathers." They are nearly all consigned to the United Kingdom and form an important part of the total supply of East Indian kips in the world's markets. Madras is not dependent on local supplies for export, as large numbers are brought down to be tanned from the Punjab,

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the United Provinces, Central India, Calcutta, and parts of the Bombay Presidency. Small tanneries are to be found in nearly every district of the Presidency, but the great bulk of the industry is concentrated round Madras, at Bangalore, Vellore, Dindigul, Coimbatore, and Trichinopoly. Fresh hides from the slaughter houses are of importance only in Bangalore and Madras. Except in large towns, and more especially in cantonments, cattle are never killed for food, the greater part of hides available being those of animals that have died from old age, disease, or injury. Conditions favoring the industry in southern India are cheapness of raw materials, an abundance of tannin-yielding plants, and cheap labor. The capital outlay involved in setting up tanneries of the local type is apparently not considerable.

Exports of tanned skins to all countries in 1915-16 increased by 8 per cent. in quantity and 11 per cent. in value. Goatskins improved by 20 per cent. in quantity and sheepskins by 3 per cent. Shipments of goatskins to the United States increased fourfold, while those to the United Kingdom declined by 21 per cent. The United Kingdom purchased sheepskins to the value of $1,580,964, the United States $637,836, and Japan $287,448. On an average of 10 years the United States has been the largest purchaser of raw goat and sheepskins from Madras and next to the largest buyer of tanned skins, being exceeded in respect to the latter only by the United Kingdom. General activity in leather-producing centers in America during the past year caused an exceptional demand for raw materials from all available sources of supply. In the case of goatskins and sheepskins the demand is said to have been particularly strong owing to greatly increased use of goat and sheep leather in shoe manufacture resulting from styles prevailing for footwear, especially for women. After importation into the United States, Madras goatskins, whether raw or in the partly manufactured state known as "tanned or dressed," are converted into finished kid leather, which product in its various forms, glazed, colored, white, or in mats, etc., brought high prices during the past year. Madras sheepskins, besides being used for shoe stock, serve as leather for book binding, fancy leather work, etc. The skin trade in the Madras Presidency is a very important one, and as the local consumption of tanned skins is much less than that of tanned hides a much larger proportion of the total yield of skins is available for export. Unlike hides the majority of skins are derived from animals that have been slaughtered for food. Besides the local supplies the Madras tanners receive large numbers from other parts of India, and from such centers as Cawnpore, Agra, Delhi, Amritsar, Sholapur, Amraoti, Hyderabad, and Poona, many thousands of skins being sent down by rail every year.

**Brazil's Exports of Goatskins.** CONSUL GENERAL ALFRED L. MOREAU GOTTSCHALK, Rio de Janeiro, in *Commerce Reports*. Brazil ships yearly some $3,000,000 worth of goatskins, the United States taking much the largest proportion of these cargoes.

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## PATENTS.

**Leather Finishing Machine. U. S. Patent 1,199,122.** FRANK F. SLOCOMB, Phila. Pa.

**Manufacture of Leather and Products Resembling Leather. U. S. Patent 1,200,146.** W. SPALTEHOLZ AND H. HARING, Germany. Hides are dehydrated and treated with a molten mass of resinous material.

**Leather Stretching Frame. U. S. Patent 1,199,756.** CHARLES BISHOP, Newark, N. J.

**Skin, Hide and Leather Working Machine. U. S. Patent 1,204,914.** FRANK WAYLAND, Salem, Mass.

**Leather Rolling and Embossing Machine. U. S. Patent 1,204,092.** CARL VOSS, Newark, N. J.

**Artificial Leather. British Patent 8,202.** W. G., L. H. AND G. R. AYRES, Third Street, Philadelphia, Pa. A core of burlap or the like has fibrous material pricked through it so that there is a layer of fibers on each side, and to one side is applied a preliminary coating of a colloidal character, preferably cellulosic. Whilst this coating is still wet, the fabric is pressed to lay the fibers at the surface, and then a final coating is applied, which may be stamped, pressed, or pebbled to imitate leather.

**Artificial Leather. British Patent 8,821.** J. CHYLIK, Krizenua, Austria. Artificial leather is made by coating canvas, etc., with a composition made by dissolving colophony in linseed-oil varnish to form a viscous paste and adding successively milk curd and slaked lime. Several thicknesses of coated fabric may be stuck together, dried, soaked in water to soften them, and then pressed into sheets. Powdered leather waste may be added, and the composition rolled into sheets.

**Tanning. British Patent 7,635.** C. V. GREENWOOD, Blundellsands, near Liverpool. Mucilaginous material is employed along with tannin, which results in shortening the time required.

**Dyeing Leather. British Patent 101,109.** A. G. BLOXAM, London. Bronze kid is prepared by dyeing the leather in a bath consisting of rosaniline and pentamethylrosaniline hydrochlorides and tannin dissolved in alcohol with addition of some nitrobenzene, and then, after smoothing, applying a topping or polish consisting of the same dyes, tannin, and shellac, dissolved in alcohol, with or without addition of some amyl alcohol. The shade produced can be varied by varying the relative proportions of the two dyes. The process may be applied to the leather, or for staining or maintaining the color of boots or shoes.

**Treating Sewage. British Patent 9,989.** G. W. AND J. F. TAYLOR, Denby Dale, England. In a sewage purification tank of the kind in which air is forced through porous tiles provided over the whole surface of the floor, the air supply is so arranged that air is delivered through one portion of the surface at one time and through the remaining portion when the supply to the first portion is cut off.

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## COMMITTEE ON ANALYSIS OF SULPHONATED OILS.

Members who are willing to serve on this committee are requested to send in their names to W. K. Alsop, Chairman, Ridgway, Pa.

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## RESEARCH LABORATORY.

At the Chicago meeting of the National Association of Tanners, November 16, the annual report of the Tanners' Institute was distributed. A review of this report will be presented in the JOURNAL next month. The Advisory Committee of the National Association of Tanners and the American Leather Chemists' Association presented a report, by which it appeared that nearly all the funds necessary to assure the inauguration of the Research Laboratory had been promised. After a statement by President Lesh in regard to the situation, additional subscriptions were asked for, and all the deficit was made up before the meeting adjourned. It would seem that the Research Laboratory can now be established with certainty of proper support for a period of at least five years.

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The Journal of the

# American Leather Chemists Association

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